TWELVE MONTH PROGRESS REPORT
NASA-NAG8-846

October 1, 1990 to November 1, 1991

CHEMICAL COMPATIBILITY OF CARTRIDGE MATERIALS

November 15, 1991

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A. Statement of the Problem

In early 1992, new crystal growth experiments will be conducted in space under zero gravity condition. These experiments will involve the growth of GaAs crystals. TZM, a molybdenum alloy containing titanium and zirconium has been selected as the cartridge material. The atmosphere within the cartridge will consist of an argon atmosphere (up to approximately 0.5 atm) with residual amounts of oxygen (up to 0.3%) and moisture.

Little, if anything, is known about the stability of GaAs in the presence of TZM. Arsenic sublimes at 613°C [1] while gallium melts at 29.78°C [1]. GaAs melts at 1236°C [2] or 1238°C [3]. Because the chemical compatibility of GaAs with TZM is not known, some potential problems may arise from the use of this combination. If the ampoule fails during the crystal growing process, the high temperature toxic components of the crystal will come in contact with the cartridge. Chemical compatibility between the crystal components and the cartridge materials must be determined to appropriately identify potential toxicity problems that could arise for the space crew. Arsenic is very toxic and when exposed to the atmosphere an oxide coating is produced [4]. The inhalation of dust and fumes must be avoided. Gallium at elevated temperature is corrosive to many metals. At low temperatures, gallium diffuses into many metals to form low melting compounds both within the grains and at the grain boundaries. If such reactions occurred between GaAs and TZM then toxic arsenic fumes could escape from the crystal growth furnace.

B. Objective

The objectives of this portion of the investigation was to study the chemical compatibility of TZM and molybdenum cartridge materials with GaAs and CdZnTe. Special emphases has been devoted to the degradation of molybdenum, TZM, and WC 103 in the presence of GaAs at 1270°C.

C. Results

For safety reasons, these studies have been be conducted under very controlled conditions. Small amounts of GaAs and CdZnTe materials must be housed in sealed containers. This task potentially involves very great health hazards which had to be overcome with simple experimental devices. The health hazards involved have dictated three different approaches to the study of chemical compatibility between the semiconductor and the cartridge materials. These approaches were (a) construction and testing of a reaction retort, (b) thermogravimetric analysis, and (c) bulk cylindrical cartridge containers. Each approach will be discussed separately including the results obtained.

1. Reaction Retort

High temperature crystal growth experiments involving GaAs will be conducted in space under zero gravity conditions. Molybdenum, with its high melting point, was initially proposed as a cartridge material for containment during melting. Because the chemical compatibility of GaAs and Mo is not known, some problems may arise from the use of such a combination. If there is a substantial corrosive reaction during the

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crystal growing process, toxic arsenic fumes could escape from the molybdenum cartridge and thus endanger the crew of the spacecraft. To study the chemical compatibility of GaAs and Mo, a high temperature retort was designed and constructed. While the retort was not to be used in the actual experiments in space, its purpose was to simulate the conditions found during the crystal growth process.

The retort was designed so that GaAs could be melted directly in a molybdenum container. The final retort design is shown in Figure 1. The molybdenum container or boat, a 0.5 mm thick foil, was resistance heated by passing an electrical current through 3.175 mm (0.125 in) diameter molybdenum rods connected to the foil. The smaller cross-sectional area of the boat compared to the rods caused resistance heating of the boat. The temperature of the boat was measured by a thermocouple touching the bottom of the boat. The Mo rods were protected from mutual contact by ceramic insulators (Figure 2).

The retort was constructed of quartz. The quartz tube did not come in contact with the heated Mo rods or boat. However, the retort vessel was of double wall construction for water cooling. The retort vessel had to be cooled for physical handling and for protect against thermal cracking of the quartz vessel which could allow arsenic vapors to escape into the atmosphere. Quartz was selected as the retort container because of its stability up to 1500°C for long periods of time. Also, quartz is transparent so that the reaction could be monitored.

Molybdenum oxides quite readily in the presence of oxygen when heated to relatively low temperatures (250°C). This oxidation is

undesirable and must be prevented. Therefore, provisions were made to evacuate the retort and back fill with argon. To eliminate as much oxygen as possible from the system, the retort was evacuated and back filled three times. On heating, the GaAs would likely decompose giving off lethal arsenic gas. To prevent the escape of these toxic fumes the retort had to be air tight. Thus, the internal argon gas was maintained at the negative pressure of 0.5 atm gage.

Compatibility tests were to be run for various times up to a maximum of 24 hours at 1270°C. However, initially, short runs of one hour were to be made so that the molybdenum boat could be examined for deterioration. If no corrosive effects of the boat were noted after 1 hour, then subsequent tests would be carried out in which the boat would be inspected after each test. The boats would be subjected to macroscopic examination and to microscopic examination using a scanning electron microscope.

After assembly of the double walled chamber, the retort was checked for leaks and was found to maintain a pressure of 0.5 atm Ar for 24 hours. Several trial runs were made using this apparatus. A number of defects in the system became evident very early in these trials. For safety reasons, all experiments had to be performed out of doors regardless of the weather. Also, problems of obtaining the desired temperature were encountered. Three heating experiments were conduced in the retort, but the maximum temperature reached was only 1140°C (See Figure 3). Only 30.5 amps was required to reach 1140°C and additional power could have been provided. The problem was "burn out" of the molybdenum boat which occurred within ten minutes.

There are two reasons for the "burn out": (a) oxidation of the molybdenum boat resulting from inadequate evacuation of oxygen from the retort, and (b) creep of the boat at high temperature. The problem with creep results from insufficient coupling between the molybdenum boat and the heating rods. The molybdenum boat was formed around the ends of the heating rods with a ceramic insulator tube slipped over the ends of the boat. The friction on the boat between the rod and the insulator tube was enough to hold the boat and make the electrical contact. On heating this friction was not enough to support the weight of the other insulators bearing on the last insulator from above (Figure 2). Also, the measurement of the exact temperature of the GaAs in the boat was difficult, if not impossible. In addition, there was the problem of leaks after a single use of the retort. The sealant used to secure the retort at points of entry (heating rod holes, vacuum lines, etc.) evidently deteriorated during the experiment. Therefore, realizing that a major redesign of the retort was necessary, which would consume a great deal of time for additional construction, this portion of the investigation was changed to use a closed furnace system.

2. Thermogravimetric Analysis

A Thermogravimetric Analyzer (TGA) was utilized for the furnace system. The purpose of a TGA system is to monitor the weight loss of a small sample (less than 300 mg) as a function of temperature (up to 1500°C) or as a function of time at a given temperature. Any atmosphere can be used. A non-oxidizing, "non-reactive" platinum crucible generally is used to hold the sample. A reaction temperature of about

1290°C with a flowing argon atmosphere was used. The heating and cooling portions of the cycle were performed at 50°C per minute. The holding time at temperature was 24 hours. A scanning electron microscope (SEM) with an Energy Dispersive X-ray Analyzer (EDX) was used to examine all samples after testing.

The first type of sample used consisted of a container of molybdenum foil folded tightly around a piece of TZM and several pieces of GaAs (Figure 4). In all cases the amount of GaAs used was 3 to 10 mg and the TZM was 5 to 7 mg. The rest of the sample weight consisted of the Mo-foil wrapping. The four samples tested are listed in Table 1.

In sample MOTZM, no attack of the Mo foil and the Pt boat occurred and no reaction between the atmosphere and the TZM was observed. However, for TA1 and TA2, a hole must have been punched in the Mo foil during the wrapping of the sample. In each case the hole allowed the molten Ga to reach and react the Pt boat. The bottom of the boats were dissolved away thus dropping the sample out of the hot zone of the vertical furnace terminating the run (Figure 5).

Sample TA3 used a W-wire basket to hold the sample in the furnace. The inside surface of the Mo foil and the surface of the TZM was bright and shiny at the end of the run. However, scanning electron microscopic examination of the sample revealed some reaction occurred between the GaAs and the TZM and the MO foil. This reaction seemed to be of a general etching type. No evidence was found by Dispersive X-ray Analysis (EDX) of either Ga or As on the surfaces of the Mo foil or of the TZM. It is not known which element, Ga or As, was responsible for the reaction which occurred. The W-wire evaporated at a rate of about 3

mg per hour and this masked-over the weight loss of the GaAs (3 mg). One hour was the estimated time for As to evaporate from the system. Without the means of electron beam welding, the Mo foil could not be sealed completely to produce a closed system. Therefore, both Ga and As were able to boil off.

Results of this type of experiment indicated that the GaAs decomposes into arsenic vapor and "molten" gallium at the temperatures involved. This produced two consequences. First, all the arsenic vaporized out and was lost to the system. X-ray analysis revealed no arsenic present after any of these runs. Second, the molten gallium tended to escape from the container and very vigorously attacked and dissolved the "non-reactive" platinum crucible (Figure 5). The presence of gallium on the remains of the platinum crucibles was found by x-ray analysis (Figure 6).

Because of the cost of platinum crucibles, tungsten wire-baskets had to be substituted for the platinum crucibles. These baskets were heavier than the platinum crucibles and, also, lost considerable weight during the heating cycle. The foil-wrapped samples were not air tight and an overall redesign of the sample had to be made. The redesigned sample was much heavier then the weight which could be monitored by the TGA. Therefore, the TGA system was used only as a controlled atmosphere furnace in which the heating, holding, and cooling cycles could be programmed.

Five experiments using a redesigned specimen configuration were performed in a TGA system (TGA) to determine the reactivity of GaAs with Molybdenum and TZM at 1280°C. All samples consisted of a small

molybdenum cylinder (3.175 mm O.D.) with a closing plug. Such a cylinder after treatment is shown in Figure 7. The cylinder contained GaAs and a piece of TZM. The weights of the TZM and GaAs were maintained between 11 to 14 mg and 13 to 17 mg, respectively. The cylinders were loaded under an argon atmosphere. The test atmosphere in all cases was flowing argon. Heating to temperature was performed at a rate of 50°C per minute. Cool down occurred at about the same rate. The five samples are listed in Table 2. The computer malfunctioned during the 18 hour run for sample MV10. The total time at 1280°C was between 10 and 15 hours but could not be determined. This experiment was performed again (MV11) but the sample was inadvertently destroyed during preparation for metallographic examination. After each run, the cylinders were cut in half and the TZM removed. The bottom half of each cylinder and the TZM were mounted and polished but not etched. The polished sections were then examined in a SEM. Photomicrographs were made to measure the depth of the diffusion zone and EDX was used to identify the various regions within the diffusion zone.

The diffusion zone as a result of the reaction of GaAs with molybdenum and TZM was found to consist of two regions, called herein the outer and inner zones. The depth of each zone and the total depth of the diffusion zone were measured. Figures 8 and 9 show the growth of these regions with time in the wall of the molybdenum cup (cylinder) and TZM, respectively. Figure 10 illustrates the general appearance of the diffusion zone. After 24 hours the diffusion zone in both the molybdenum and TZM was on the order of about 0.02 mm thick. The wall thickness of the TZM tube intended for use in space was on the order of 0.6858 mm

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(0.027 in). Thus, in 24 hours about 29 or 30% of the wall thickness was attacked during the reaction of GaAs with molybdenum or TZM.

Note that Figures 8 and 9 are plots of log depth vs. linear time. The data does not fit a standard log-log plot and, thus, does not seem to adhere to the standard square root of Dt diffusion law (D is the diffusion coefficient and t is time). This may be the result of cracking of the diffusion zone every 0.05 to 0.25 mm along its length. This cracking extends through the diffusion zone to the base metal as shown in Figure 10. This cracking should allow new reaction surfaces to be present at all times thus increasing the reaction rate.

Through the use of EDX, the various regions of the diffusion zone were identified. In all specimens, whether molybdenum or TZM, the outer zone was found to contain arsenic and molybdenum while the inner zone contained arsenic, gallium and molybdenum. These zones were relatively ease to identify because each zone consisted of very large crystals or grains. The boundary between these grains was the boundary between the inner and outer zones. The boundary between the inner zone and the base metal was in all cases a line of voids created through vacancy diffusion. The identification of gallium in the inner diffusion zone and not the outer zone indicated that gallium attacks molybdenum at a faster rate than arsenic.

Figure 11 shows the plug end of the cylinder from Figure 7. No cracks in the molybdenum cylinder were evident in either Figure 7 or Figure 11. Tungsten was found on the outer surface of the cylinder after treatment (Figure 12). This tungsten is the result of vaporization of the tungsten wire-basket.

a. Molybdenum and GaAs: To analyze what occurred between the TZM and GaAs (also between molybdenum and GaAs), the cylinder was broken open mechanically. The cylinder fractured in a brittle manner as can be seem in Figure 13. This figure shows the bottom end of the cylinder, the bottom of the plug and part of the cylinder wall from the top portion of the cylinder.

Figure 14 shows the microstructure of the bottom of a plug used in a cylinder which was tested without GaAs. Oxidation of the cap and the presence of small size porosity voids can be seen. Figure 15 is the x-ray spectrum taken from the surface in Figure 14. Only molybdenum was found. Figure 16 shows the microstructure of the bottom of the plug from Figure 13. The molybdenum of the plug has been attacked as can be seem by the grain structure. EDX analysis of the cap showed molybdenum and arsenic (Figure 17). However, two somewhat larger crystals can be seen in the center of Figure 16. Both of these crystals were found to be gallium (Figures 18 and 19). The x-ray spectrum (Figure 20) from the region between the two particles again indicates molybdenum and arsenic.

The structure of the inside wall surface of an unused (not heated) molybdenum cylinder is shown in Figure 21. This is a "machined" surface. The x-ray spectrum for this material is found in Figure 22. The structure of the inside cylinder wall after reacting with GaAs is shown in Figures 23 and 24. Comparison of Figures 23 and 24 with Figure 21 indicates that some reaction occurred between the molybdenum cylinder and the GaAs. EDX analysis of the inside surface of the cylinder wall shown in Figure 13 revealed only molybdenum (Figure 25) at the end which was in contact with the end plug and, therefore, was protected from the

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GaAs. Further down the wall, arsenic was found again (Figure 26). No gallium was found.

The general x-ray spectrum of the molybdenum cylinder wall from the area of Figure 23 is shown in Figure 27. Again, only molybdenum and arsenic were detected. However, x-ray spectra of various particles seen in Figure 23 revealed the presence of other elements. Some of these very small particles contained tungsten (Figure 28). Actually, the particles were small enough so that the beam penetrated to the underlying wall where the molybdenum and arsenic peaks were produced. The particles very likely are tungsten oxide dust which was torn loose from the outside cylinder surface when the cylinder was mechanically broken open.

In an effort to find gallium on the wall surface, an x-ray spectrum was produced at a magnification of 25,000X at the intersection of three grains. This spectrum is shown in Figure 29. Gallium was not detected in the grain boundary region. Another region of the wall was then analyzed (Figure 30). Considerable porosity along with small particles were found. EDX analysis of some of these particles revealed the presence of both gallium and titanium (Figure 31). The titanium must be the result of the presence of TZM within the cylinder.

The structure at the bottom of the molybdenum cylinder (Figure 32) again indicates that a reaction occurred between the molybdenum and the GaAs. An x-ray spectrum (Figure 33) of the cylinder bottom shows the presence of mainly molybdenum. The tungsten if presence would be dust as explained above. Various types of particles were found on the cylinder bottom. Some were molybdenum (Figure 34); some contained

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molybdenum with arsenic and a small amount of gallium (Figure 35). Other small particles contained a large amount of gallium and titanium (Figure 36). These may have come from the surface of the TZM.

Figure 37 shows the brittle fracture surface of the cylinder wall resulting from mechanically breaking the cylinder. Three zones in the wall are evident from this figure. The first zone at the outside surface shows a fine grain structure and is about 100 μm thick. EDX analysis revealed that this zone contained both molybdenum and tungsten (Figure 38). The second zone contains a large grained microstructure consisting of only molybdenum (Figure 39). The third zone is about 10 μm thick at the inside wall of the cylinder. EDX analysis of this very fine grained region showed the presence of some arsenic (Figure 40).

b. TZM and GaAs: The reaction between TZM and GaAs was very similar to that between molybdenum and GaAs. The microstructure (Figure 41) and the x-ray spectrum (Figure 42) of TZM heated for 24 hours without the presence of GaAs are given for comparison purposes. Only the molybdenum peak is evident. The TZM after reacting with GaAs is shown in Figure 43 while Figure 44 shows the microstructure of this TZM. EDX analysis of the surface (Figure 45) revealed some gallium along with titanium. Titanium was found only in the x-ray spectrum after the surface reaction with GaAs.

Figures 46, 47 and 48 are x-ray spectra of particles shown in Figure 44. These particles ranged from pure molybdenum (TZM) to high concentrations of gallium. The microstructure in Figure 49 is a high magnification of the center of Figure 44. The x-ray spectra from three

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particles shown in Figure 49 are given in Figure 50, 51 and 52. All of the particles contained gallium and titanium. However, when x-ray analysis (Figure 53) was performed of the matrix (a grain) from the center of Figure 49 only a molybdenum peak was found.

Even though arsenic was found on all internal surfaces of the cylinder, gallium was found only in three places: as crystals on the bottom of the plug, within very small titanium-rich particles at the bottom of the cylinder, and in small particles on the internal surface of the TZM. These results indicate that GaAs dissociates into gallium and arsenic during the heating cycle. The arsenic vaporizes and generally coats the surface of the molybdenum cylinder and the TZM block. The gallium melts and must sputter within the cylinder for some to reach the end plug. It is believed that the gallium also attacks the grain boundaries of the molybdenum and the TZM. This causes the etched effect of the molybdenum cylinder wall.

3. Bulk Cartridge Containers

a. Samples Sectioned Parallel to Cylinder Axis: Additional experiments were run with GaAs at 1260°C (24 hours) in a TZM capsule with a molybdenum plug. The heat treating cycle was as close as possible to that cycle given for GT-SCI-1 (GTE-1c) for GaAs (Figure 54). The experimental procedure for the manufacture of the TZM capsule and the heat treatment cycle used are listed below. The capsule was loaded in a vertical tube furnace under an argon atmosphere. The heat treating atmosphere was flowing argon.

The capsule was manufactured by cutting a 9.52 mm (3/8-inch) thick

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disc from a 25 mm (1-inch) diameter solid rod of TZM. This disc was cut into pie-shaped quarter sections. A hole 5.556 mm (7/32-inch) in diameter and 6.35 mm (1/4-inch) deep then was drilled in the center of each section. A molybdenum plug was machined to fit this hole and to fit about 3.175 mm (1/8-inch) deep into the hole. This produced a cavity of about 5.556 mm (7/32-inch) diameter by 3.175 mm (1/8-inch) deep (about 0.61 cm^3) to be filled with the semiconductor material.

The heat treatment cycle consisted of heating at a rate of 5°C/min from room temperature to 1260°C. That is, starting at 0 time to 252 minutes (4.2 hrs). This temperature was held for a total of 888 minutes from the 252 minute time to 1140 minutes (14.8 hrs). Cooling from 1260°C to 160°C was performed at a rate of 2°C/min from the 1140 minute time to 1690 minutes (550 minutes = 9.17 hrs). The total treatment time was 1690 minutes or 28.17 hours (4.2 + 14.8 + 9.17 = 28.17 hrs. = 28 hours 10 minutes).

The weight of GaAs used was 260 mg. After treatment the capsule was sectioned, mounted, polished and then examined using an optical microscope with a calibrated eyepiece. The average depth of total diffusion zone of GaAs into the TZM was 0.145 mm. The variation in depth of the diffusion zone was 0.111 mm to 0.179 mm. Some type of deposit was found on the inside of the capsule after sectioning. The deposit likely was GaAs but was not analyzed.

i. TZM and CdZnTe: The initial experiment involving CdZnTe was conducted as follows. The experiment was run at 1170°C (96 hours) in a TZM capsule with a molybdenum plug. The heat treating cycle was as

close as possible to that cycle given for GCRC-SCI-3 (GCRC-7) for CdZnTe (Figure 55). The experimental procedure for the manufacture of the TZM capsule was described above for the GaAs tests. The heat treatment cycle used is listed below. The capsule was loaded in a vertical tube furnace under an argon atmosphere. The heat treating atmosphere was flowing argon.

The heat treatment cycle consisted of heating at a rate of 2°C/min from room temperature to 1170°C. That is, starting at 0 time to 588 minutes (9.8 hrs). This temperature was held for a total of 4662 minutes from the 588 minute time to 5250 minutes (77.7 hrs). Cooling from 1170°C to 170°C was performed at a rate of 1.82°C/min from the 5250 minute time to 5800 minutes (9.17 hrs). The total treatment time was 5800 minutes or 96.67 hours (9.8 + 77.7 + 9.17 = 96.67 hrs. = 96 hours 40 minutes).

The weight of CdZnTe used was 258.3 mg. After treatment the capsule was sectioned, mounted, polished and then examined using an optical microscope with a calibrated eyepiece. The average depth of total diffusion zone of CdZnTe into the TZM was 0.072 mm. The variation in depth of the diffusion zone was 0.059 mm to 0.084 mm. Some type of deposit was found on the inside of the capsule after sectioning.

ii. WC 103 and GaAs: The initial experiment with WC 103, a Nb-10Hf-1Ti alloy, was run with GaAs at 1260°C (28.17 hours) in a TZM capsule with a molybdenum plug. The heat treating cycle was as close as possible to that cycle given for GaAs (Figure 54) as described above. The experimental procedure for the manufacture of the TZM capsule was also

described above for the TZM capsules. The capsule was loaded in a vertical tube furnace under an argon atmosphere. The heat treating atmosphere was flowing argon. The cylider cavity was filled with GaAs and a piece of WC 103. The WC 103 piece was cut from a tube with a wall thickness of 0.68 mm (27 mils).

The EDX spectrum taken from the center of the cross section of the reacted piece of WC 103 is shown in Figure 56. From this spectrum, it is evident that both gallium and arsenic are present at this point along with the alloying elements niobium, hafnium and at times titanium. Prior to the reaction the cross section of the piece of WC 103 used was rectangular. After the reaction, the cross section at best could be said to be oblong in shape with EXTREMELY rough and irregular surfaces. No place in this cross section was a gallium - arsenic free zone found. In fact, large particles of relatively pure gallium were found in some regions of the cross section. These results indicate that GaAs is very reactive with WC 103. It should be remembered that the compatibility test was performed in such a manner that the reaction occurred simultaneously on all surfaces of the piece of WC 103. To obtain a true picture of the reaction rate of GaAs with WC 103, a solid piece of WC 103 in which a hole could be drilled and the GaAs added to the hole so the reaction could occur only on one surface would be best.

b. Summary of Vertically Sectioned Samples: At this point a summary is necessary for the experiments in which the samples were sectioned parallel to the cylinder axis (sectioned vertically). Figure 57 shows specimen configuration after sectioning. The reaction zone was then

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measured along the edge of the cavity.

i. TZM and GaAs: Figure 58 shows a typical reaction zone between TZM and GaAs for a heat treatment time of 13.37 hours. This was the time required only for heating to 1260°C and cooling down to 160°C as prescribed by the heating cycle given in Figure 54. Figure 59 shows the same combination after 28.17 hours. The thickness of two zone observed zones are shown along with the elements found in those region with the use of EDX. Table 3 gives a summary of the results found in three TZM - GaAs samples.

ii. WC 103 and GaAs: Figure 60 shows the cross section of a vertically sectioned WC 103 - GaAs sample after the 28.17 hour heat treatment. The reaction zones for this sample are shown in Figure 61. Table 4 summarizes the results obtained from this sample.

iii. TZM or WC 103 with CdZnTe: Figure 62 shows a typical cross section of the reaction zone between TZM and CdZnTe after a heating cycle of 96.67 hours as discussed in Figure 55. The photomicrograph at the bottom is an enlargement of an area near the reaction zone/base metal interface in the upper photo. Notice that molybdenum has diffused into the CdZnTe and CdTe has reacted with the TZM. Table 5 contains the summary of results from this sample. The reaction zones in this sample seem to be separated from the base metal. Thus no measurement could be made of the reaction zone thickness.

Figure 63 shows the reaction zone for a WC 103 - CdZnTe sample

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after a 96.67 hour heat treatment cycle. The numbered points show the elements found by EDX. Table 5 summarizes the results from this sample.

c. Summary of Samples Sectioned Normal to the Cylinder Axis: A problem was encountered with the vertically sectioned samples. The ability to determine the exact thickness of the reaction zone depended on the position of the vertical cut through the cylinder. If this cut was not exactly along the axis the thickness of the reaction zone appeared to be larger. To minimize the error in measuring the thickness of the reaction zone, a new method was used. Each cylinder was sectioned normal to the axis of the cylinder. Thus, the reaction zone and the reaction chamber appeared as circles. A typical cross section is shown in Figure 64. The radius of the circular interface between the reaction zone and the unreacted base metal in each case was determined by measuring 10 points about the circumference of the circle. The radius of each circle was then determined by a series solving 10 sets of three simultaneous equations and then averaging the results. This method is very good for determining the average value of degradation. The following three assumptions were made during this analysis: (a) the reaction occurs uniformly about the wall surface of the cylinder; (b) the amount of degradation of the base metal is the average measured cylinder radius of the reacted base material minus the radius of the unreacted cylinder hole (average radius = 2.864 mm); and (c) the percent thickness of the base material degraded is the value from 2 above divided by 0.6858 mm (0.027 inches) which is the selected cartridge tube thickness. The following results were obtained.

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Sample	Radius (mm)			Degradation of Base Metal (mm)			
	Max.	Min.	Ave.	Max.	Min.	Ave.	%
TZM	3.412	2.860	3.057	0.548	79.9	0.192	28.1
WC 103	3.207	3.126	3.190	0.343	50.0	0.326	47.5

D. Conclusions

The following conclusions can be drawn from this study of chemical compatibility of GaAs and CdZnTe with TZM and WC 103. The reaction rates with TZM were not nearly as great as they were with WC 103. The reaction between GaAs and WC 103 was almost twice that with TZM. It is expected that the same likely is true for the CdZnTe. Even though WC 103 is easier to fabricate than TZM, problems with the use of WC 103 as a cartridge material may occur. At least half of the WC 103 tube thickness will be degraded if contact is made with one of these semiconductor materials and this could cause a major loss of strength properties.

E. References

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Table 1. Molybdenum foil samples for thermogravimetric analysis.

Sample Name	Sample Contents	Foil Wrap Used	Sample Holder	Holding Temperature (°C)	Holding Time
MOTZM	TZM	Mo	Pt boat	1320	60 min.
TA1	TZM + GaAs	Mo	Pt boat	1290	42 min.
TA2	TZM + GaAs	Mo	Pt boat	1290	36 min.
TA3	TZM + GaAs	Mo	W basket	1325	24 hrs.

Table 2. Thermogravimetric samples used in this study and the measured thickness of the various region of the diffusion zone.

Specimen	Atm.	Time hr	Outer Zone mm	Inner Zone mm	Total Zone mm
MV7-cup	argon	24	0.09	0.1	0.19-0.195
MV7-TZM	argon	24	0.16	0.04	0.19-0.20
MV8-cup	argon	12	0.021	0.008-0.01	0.024-0.029
MV8-TZM	argon	12	0.011-0.015	0.006-0.009	0.018-0.024
MV9-cup	argon	6	0.006-0.007	0.0038-0.006	0.012-0.013
MV9-TZM	argon	6	0.006-0.009	0.006-0.008	0.014-0.018
MV10	argon	18	Computer malfunctioned.		
MV11	argon	18	Sample inadvertently destroyed.		

Table 3. Summary of chemical compatibility results for vertically sectioned TZM - GaAs samples.

Base Metal	Metal Matl & wt.	Reaction Zones (mm) 1*	Reaction Zones (mm) 2	Heat Treating Cycle Heating	Hold	Cooling	Total
TZM	GaAs 0.2374g	0.012	0.031	4.2h	0	9.17h	13.37h
TZM	GaAs 0.287g	0.013	0.067	4.2h	6.13h	9.17h	19.5h
TZM	GaAs 0.265g	0.040	0.057	4.2h	14.8h	9.17h	28.17h

TZM

Zone 1
Mo + Ga
-----------   Zones as shown in Figure 59.
Zone 2
Mo + As
Ga + As
UUUUUUUUUUU
Cavity

* Zone next to base metal

Table 4. Summary of chemical compatibility results for vertically sectioned WC 103 - GaAs samples.

Base Metal	Metal Matl & wt.	Reaction Regions (mm)			Heat Treating Cycle			
		1	2	3*	Heating	Hold	Cooling	Total
WC 103	GaAs 0.4265g	0.091	0.487	0.288	4.2h	14.8h	9.17h	28.17h

<pre>
          WC 103
─────────────────────
        Region 3
    Nb + little Ga
- - - - - - - - - - - - - - - - - - - -
        Region 2
  Nb + little more Ga
   + much less As
- - - - - - - - - - - - - - - - - - - -
        Region 1
  Nb + As + little Ga
- - - - - - - - - - - - - - - - - - - -
      Ga + As

UUUUUUUUUUUUUUUUUUUUUUU
        Cavity
</pre>

* Region next to base metal.

22

Table 5. Summary of chemical compatibility results for vertically sectioned TZM - CdZnTe and WC 103 - CdZnTe samples.

Base Metal	Metal Matl & wt.	Reaction Zones (mm) 1*	2	3	Heat Treating Cycle Heating	Hold	Cooling	Total
TZM	CdZnTe 0.2481g	No reaction zone (see text)			9.8h	77.7h	9.17h	96.67h
WC 103	CdZnTe 0.4612g	0.038	0.79	0.088	9.8h	77.7h	9.17h	96.67h

___TZM___
- - - - - - - - - - -   --- This region seemed to be not in
Cd + Te + Mo   contact with the base metal.

UUUUUUUUUUU
   Cavity

_____WC 103_____

    Zone 1
 Nb + Te + Cd

- - - - - - - - - - - - - - - -
   Zone 2
   Cd + Te
- - - - - - - - - - - - - - - -
   Zone 3
   Nb + Te
- - - - - - - - - - - - - - -   *ZONE NEXT TO BASE METAL

    Cd + Te

UUUUUUUUUUUUUUUUU
   Cavity

23

Thermocouple

Molybdenum heating rod

Vacuum line

Ar gas line

Pressure gauge

Rubber stopper

Water out

Quartz insulator plate

Water in

Molybdenum foil vessel

Height = 20 Inches
Inner chamber diameter = 32 mm
Outer chamber diameter = 45 mm
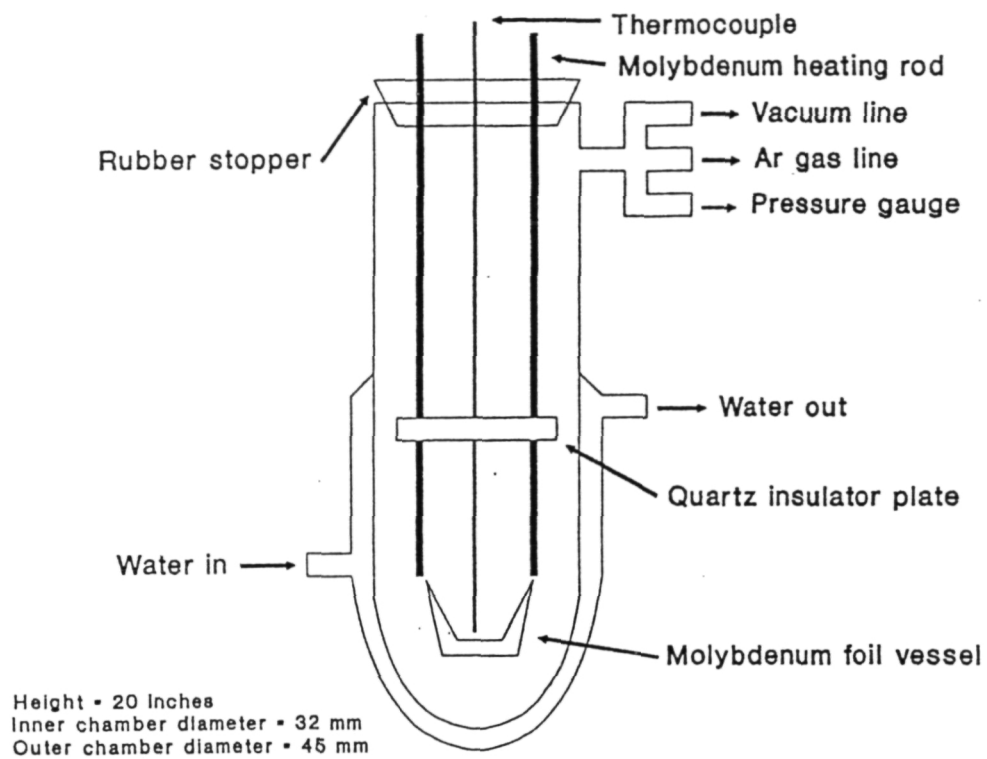
Figure 1.   Schematic of GaAs - Mo reaction retort.

Molybdenum
heating rod

Ceramic Insulator

Molybdenum
foil vessel
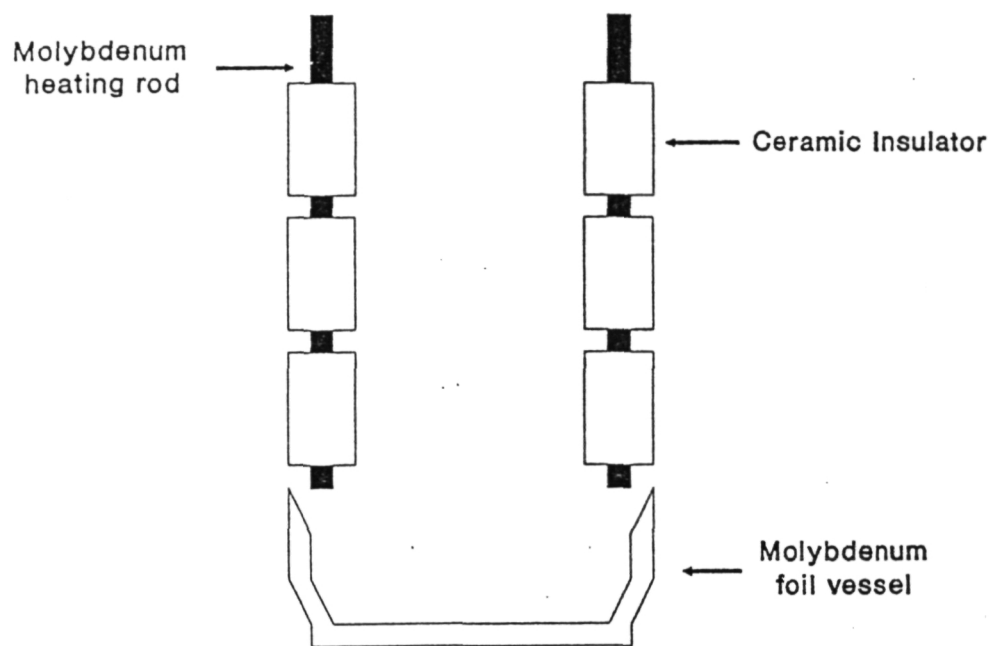
Figure 2.   Enlarged schematic of molybdenum boat and electrical
connections within the reaction retort.

High Temp Oven
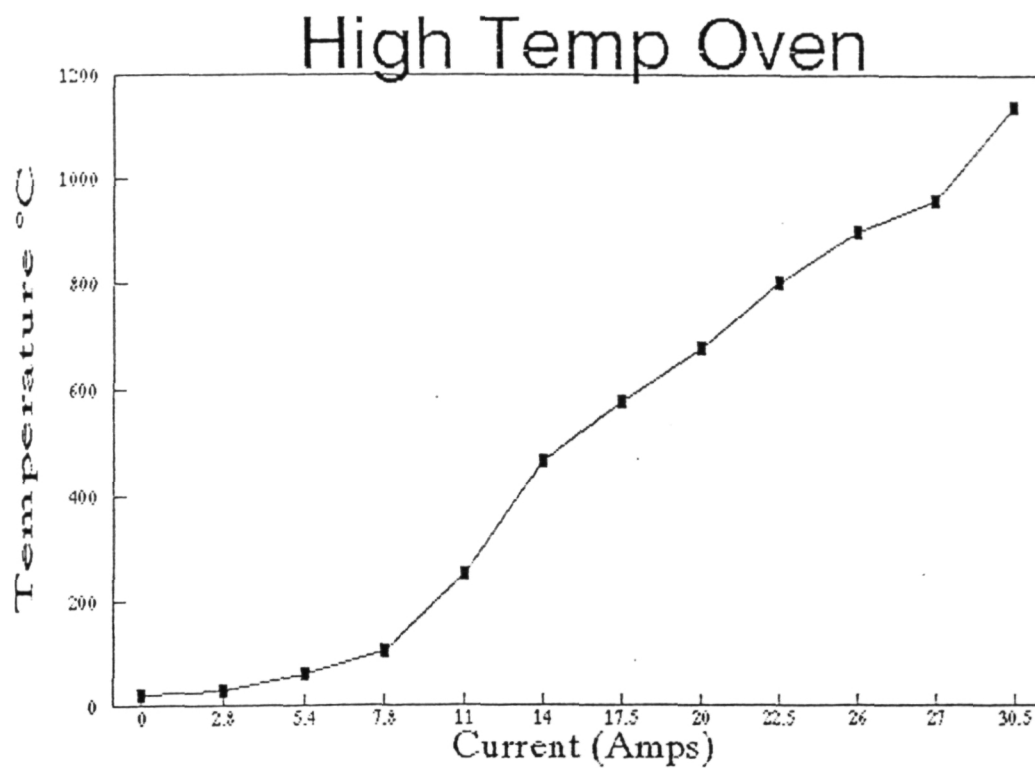
Figure 3. Reaction temperature as a function of the input current for the retort.
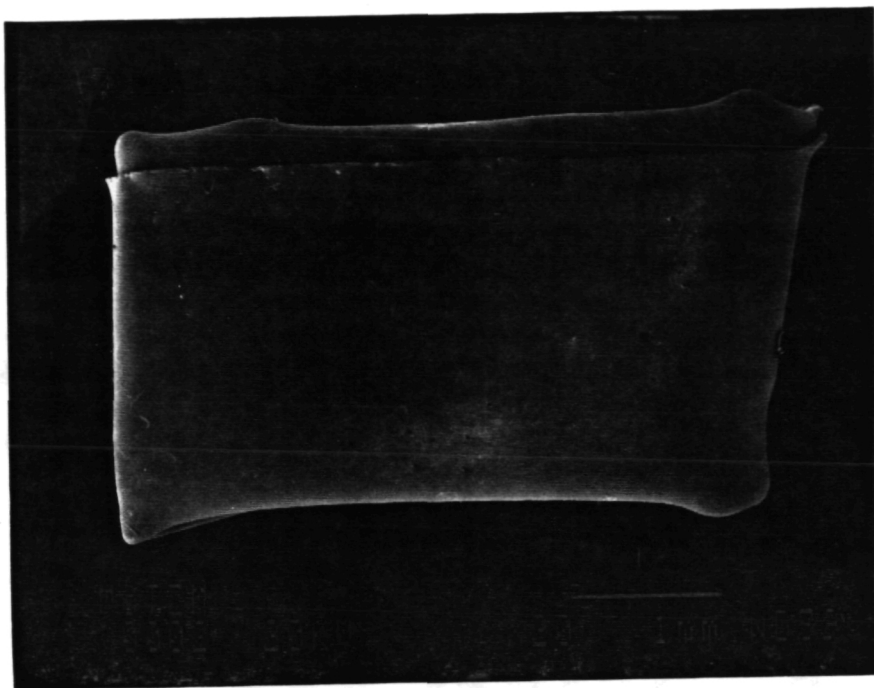
Figure 4.   Molybdenum foil container.
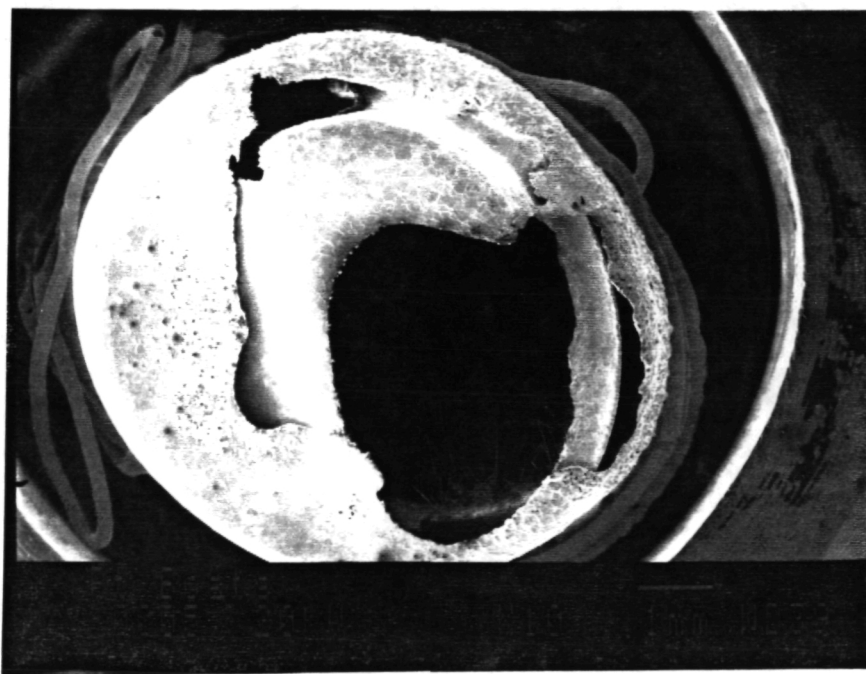
Figure 5.   Platinum boats showing attack by gallium.

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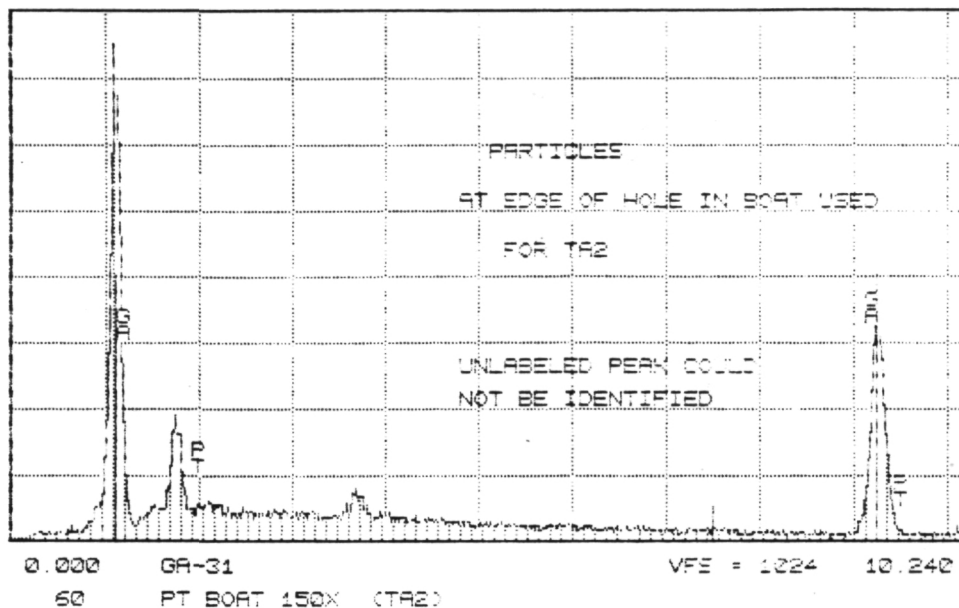
Figure 6. EDX spectrum from Ga particles shown in Figure 5.
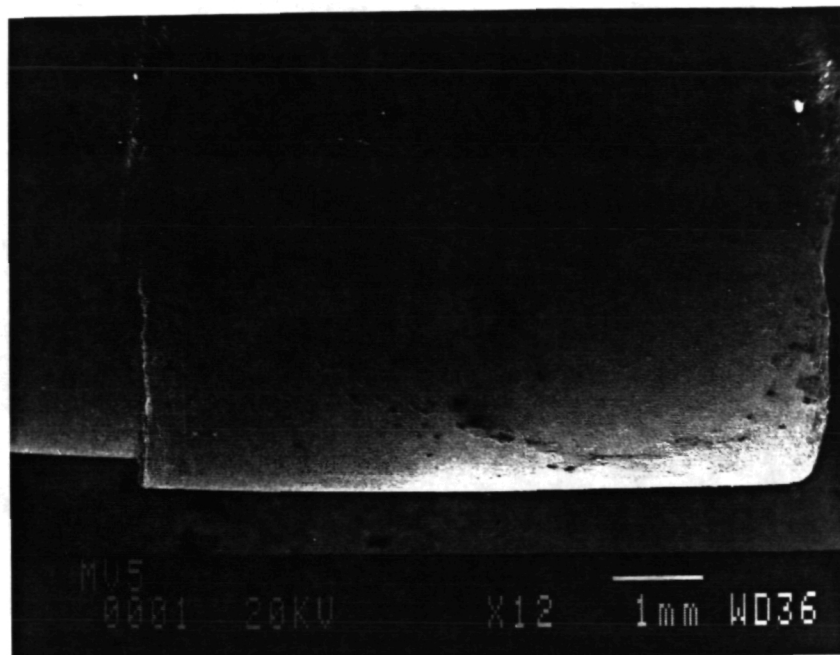
Figure 7. General view of molybdenum cylinder with plug after 24 hour reaction with GaAs.
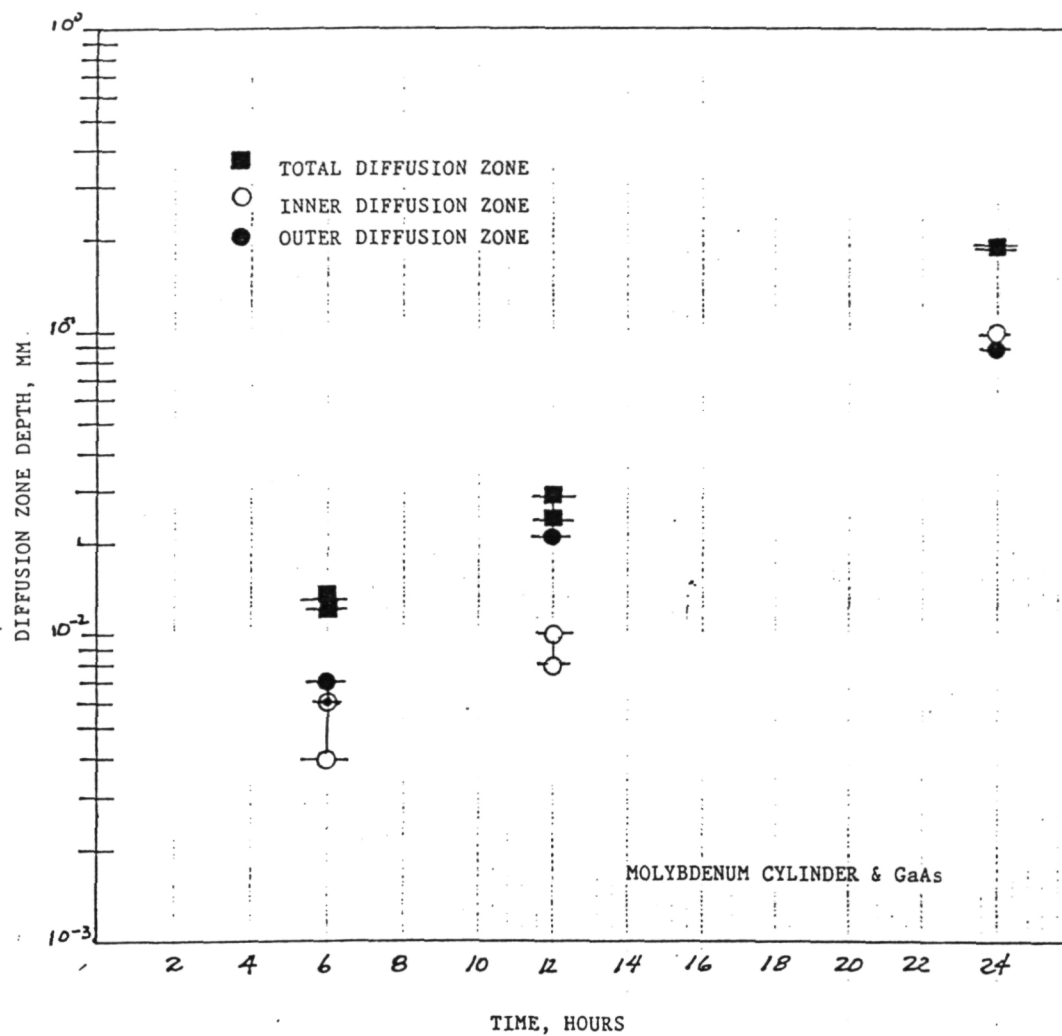
Figure 8. Depth of reaction (diffusion) zone in the molybdenum cylinder.

30
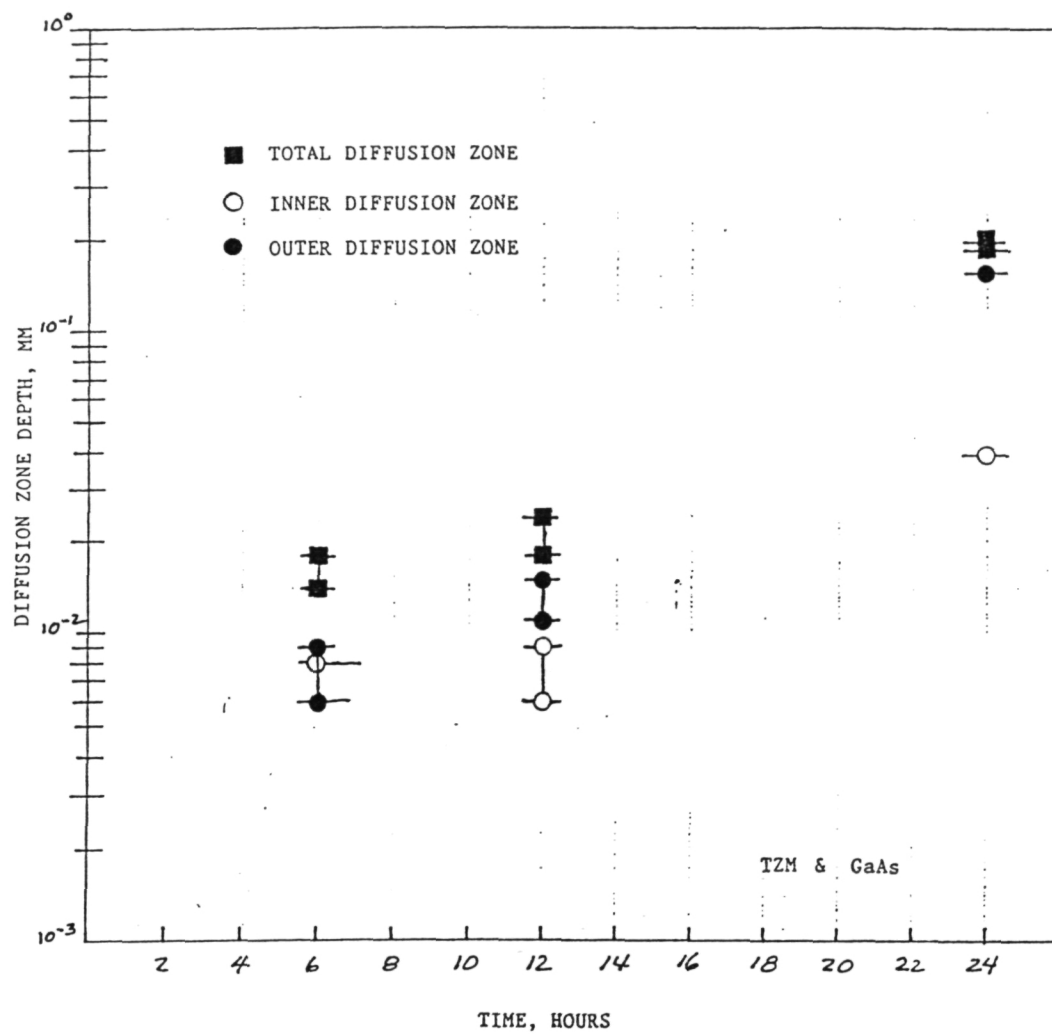
Figure 9.   Depth of reaction (diffusion) zone in the TZM with GaAs.

31
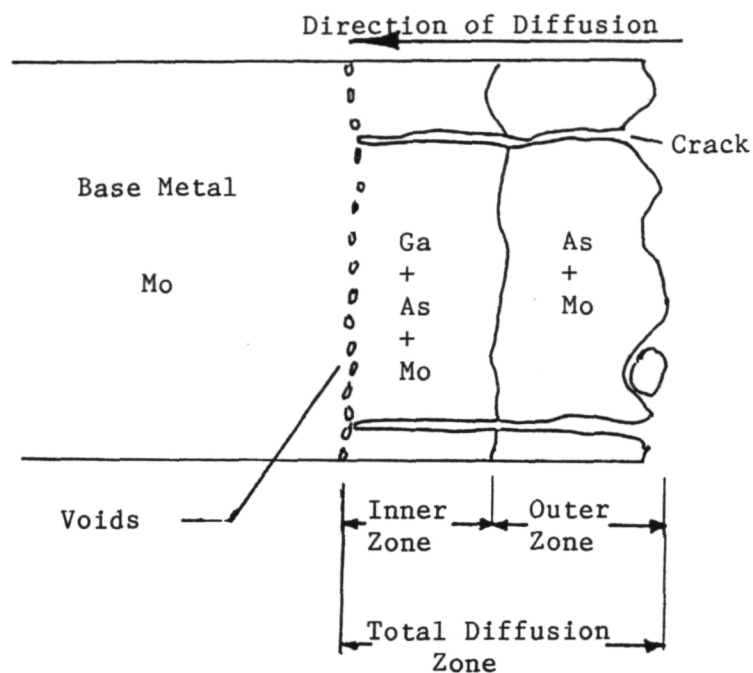
Figure 10. Reaction regions found after the reaction of GaAs with either molybdenum or TZM.
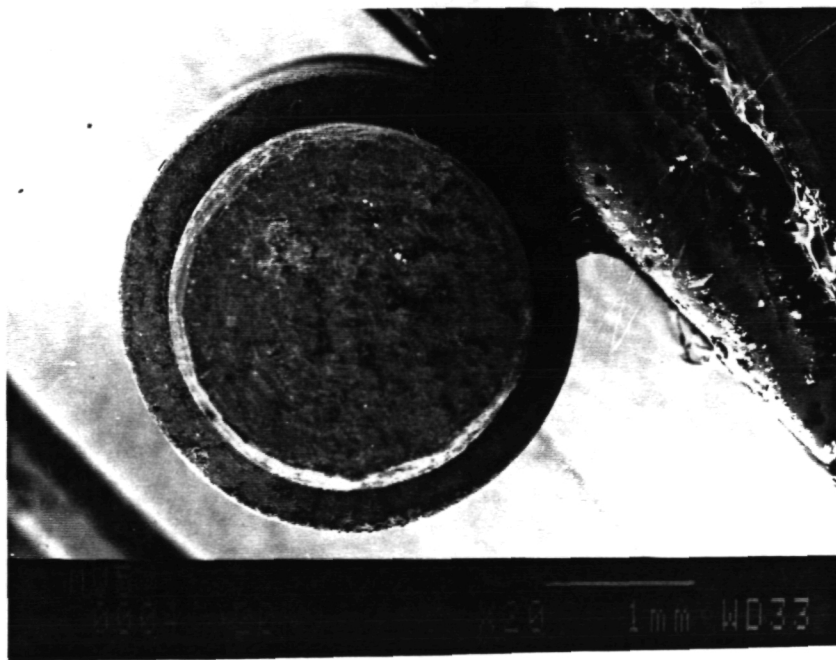
Figure 11. General view of plug end from Figure 7.
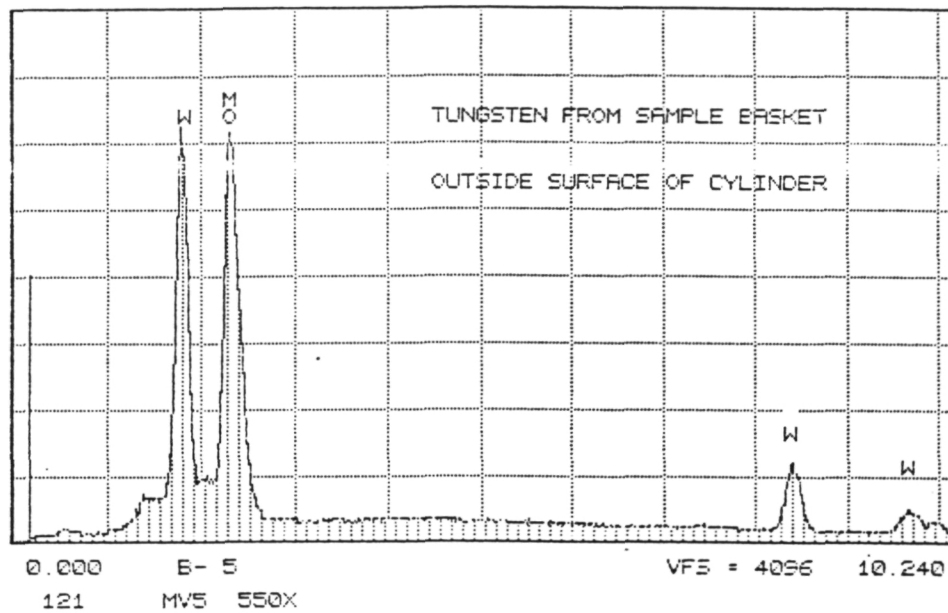
Figure 12.   EDX spectrum of outside cylinder surface.
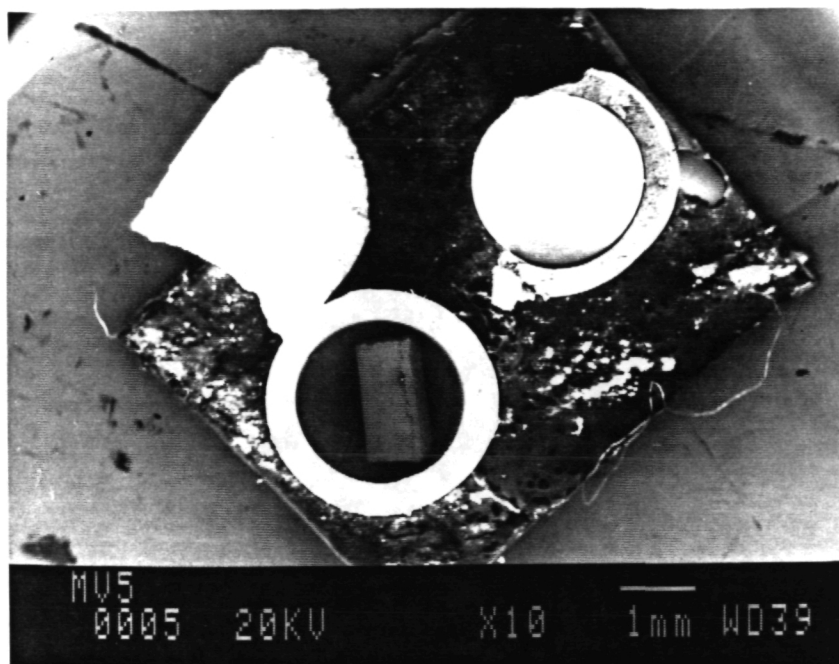
Figure 13. View of reacted cylinder after being mechanically broken apart.
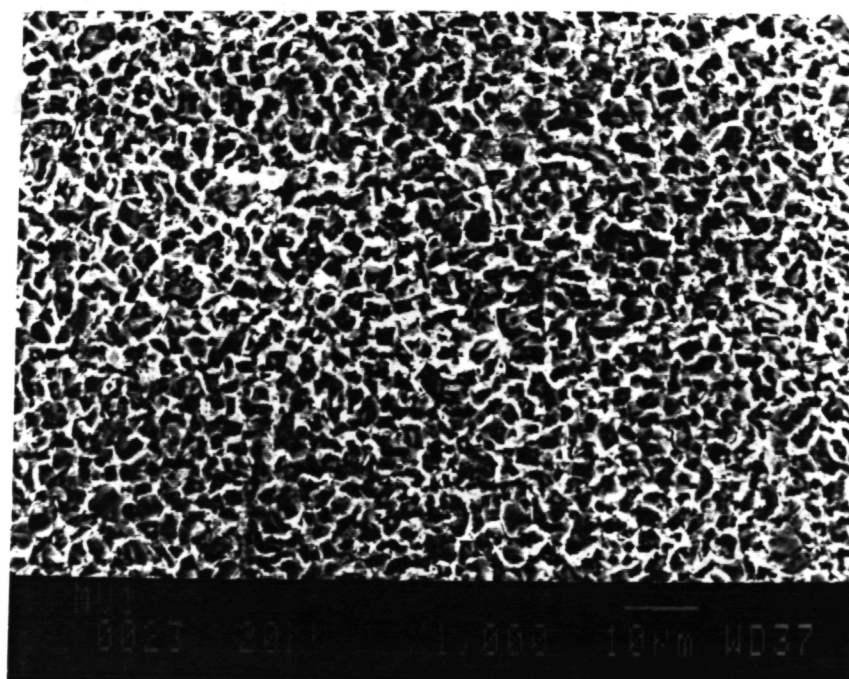
Figure 14. Surface of bottom of a molybdenum cap after 24 hour treatment without GaAs.

```
                    NO GaAs USED

              M        TREATED 24 HOURS
              O




         G A                    I  I              G
         A S                    I  I              A

0.000      B- 5                           VFS = 4096    10.240
   60      MV1    BOTTOM OF CAP 500X
```
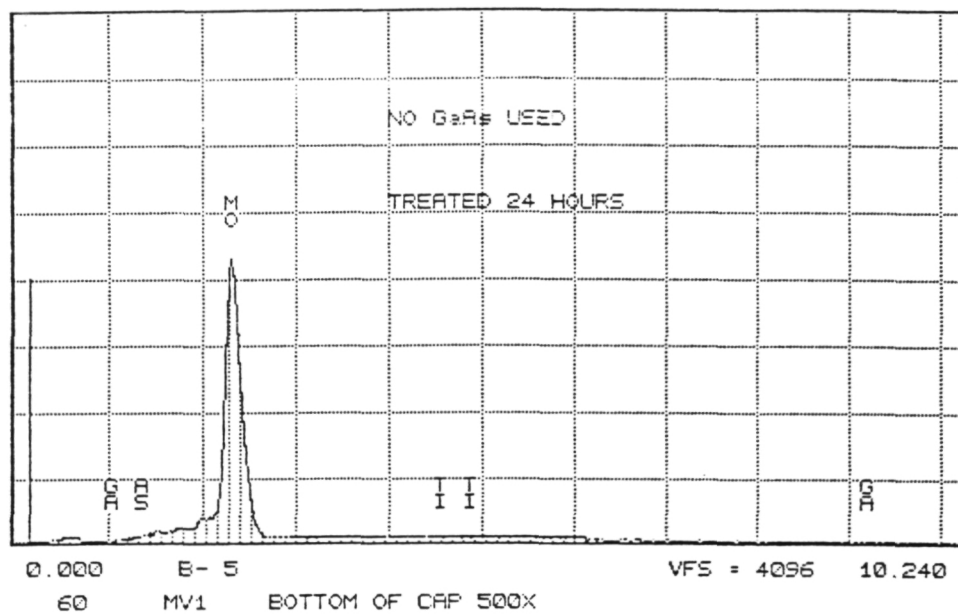
Figure 15.   EDX spectrum of surface shown in Figure 14.
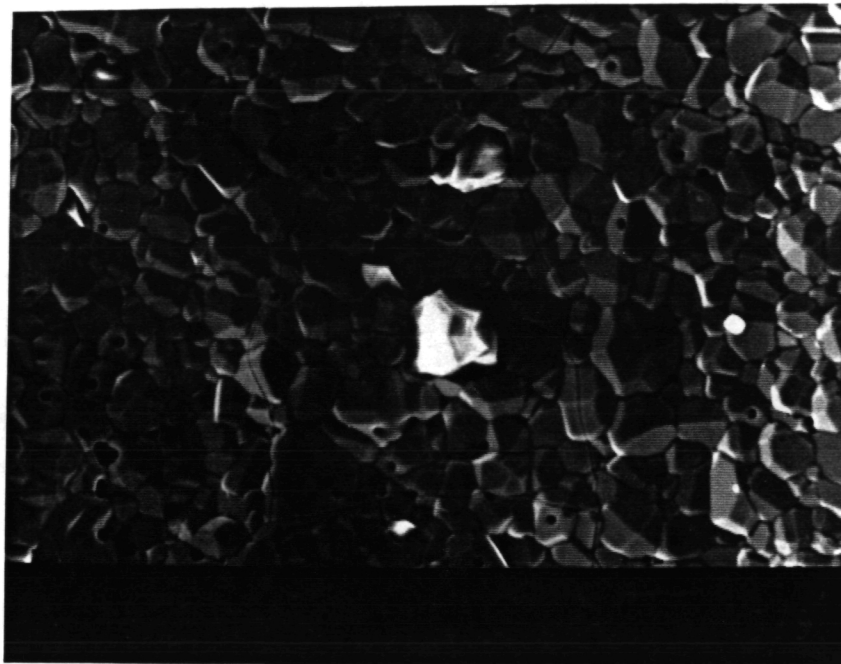
Figure 16.   Microstructure of cap after 24 hour reaction with GaAs.
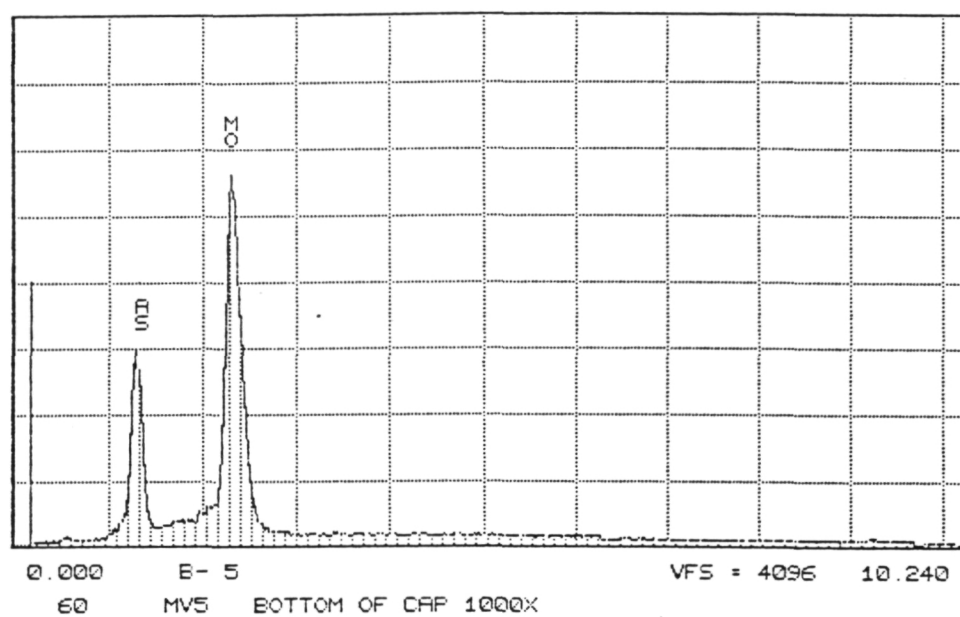
Figure 17. EDX spectrum of surface in Figure 16.

Figure 18. EDX spectrum from particle found in Figure 16.

TN-5500   MON 15-APR-91 16:49
Cursor: 0.000keV = 0
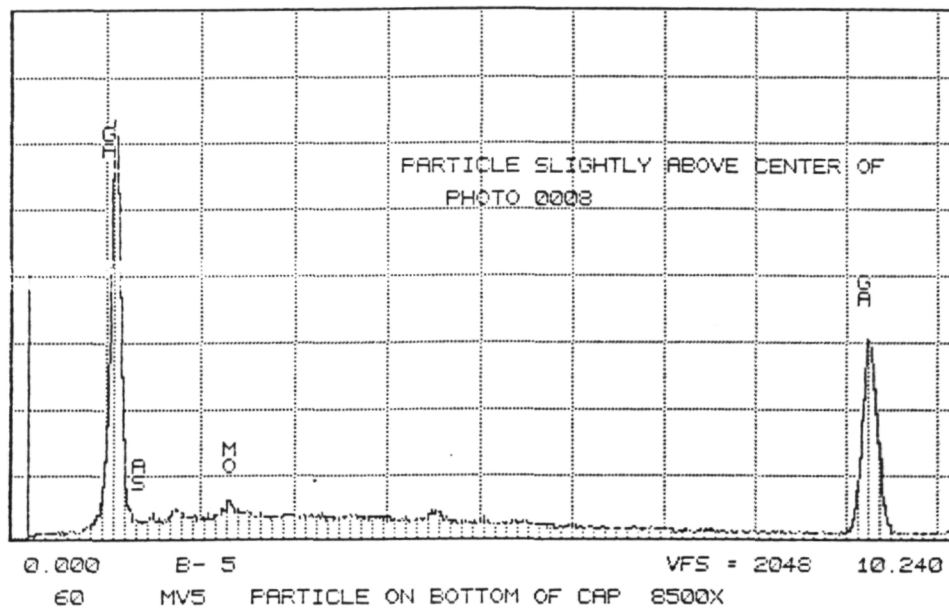
Figure 19.   EDX spectrum from particle found in Figure 16.

TN-5500   MON 15-APR-91   16:54
Cursor: 0.000keV = 0
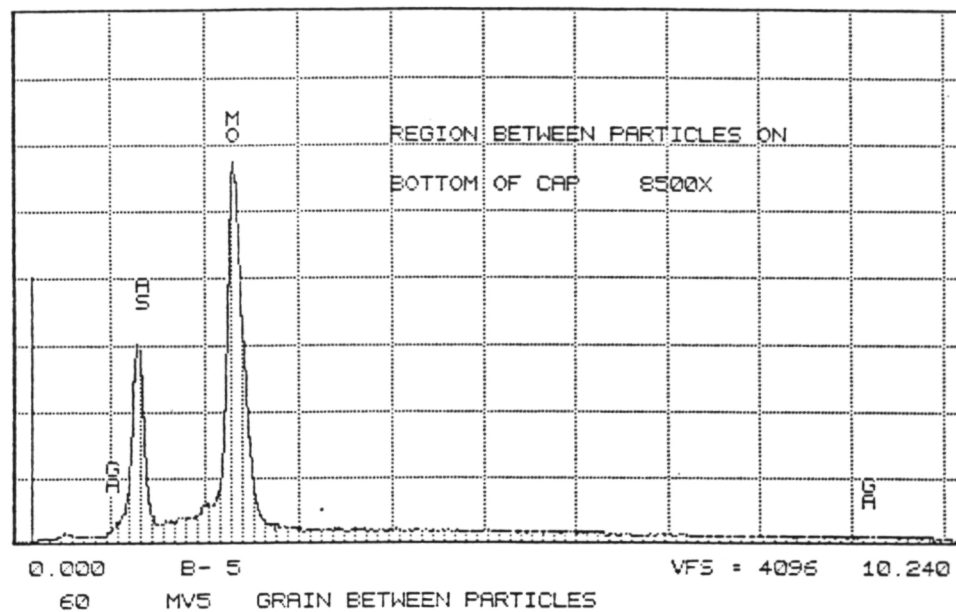
Figure 20.   EDX spectrum from region between particles found in Figure
16.
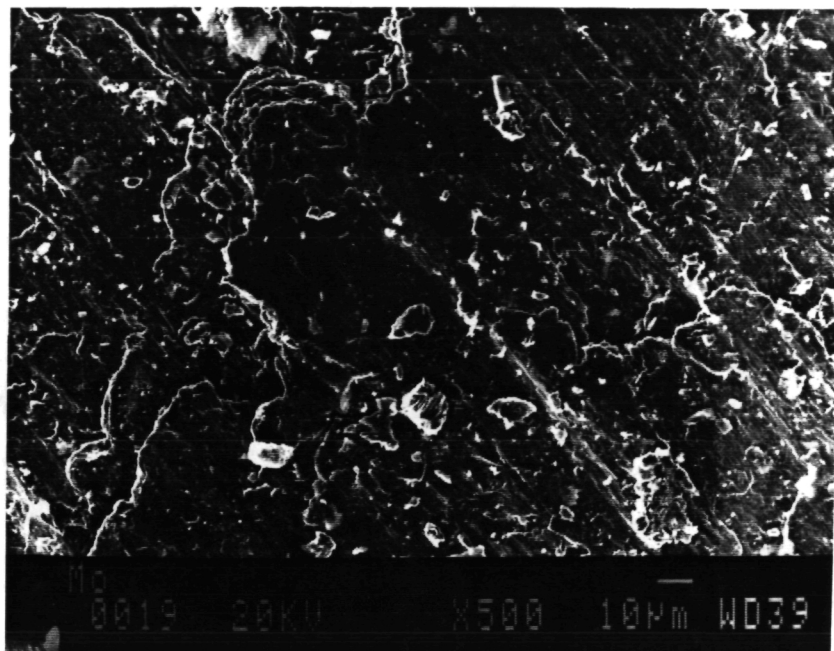
Figure 21.   Wall surface of unused molybdenum cylinder.

0.000   B- 5   VFS = 1024   10.240
    60   UNUSED MO CYLINDER   500X
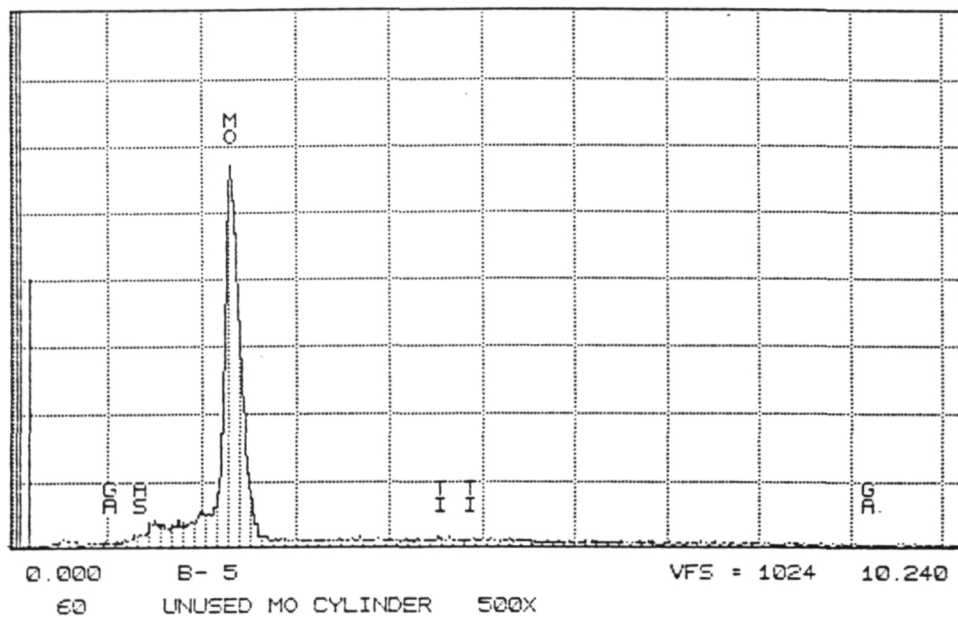
Figure 22.   EDX spectrum of surface from Figure 21.
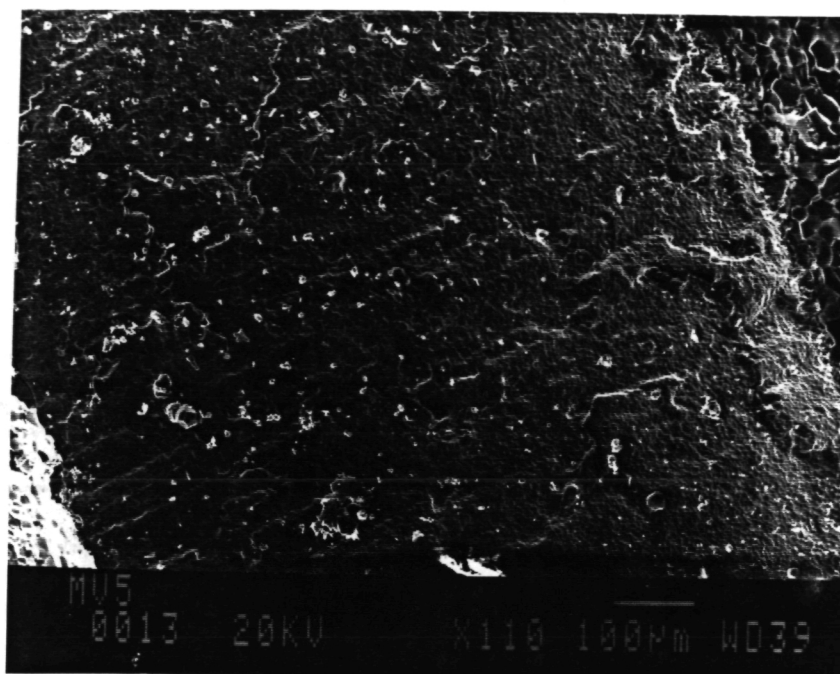
Figure 23. Wall surface of reacted molybdenum cylinder.
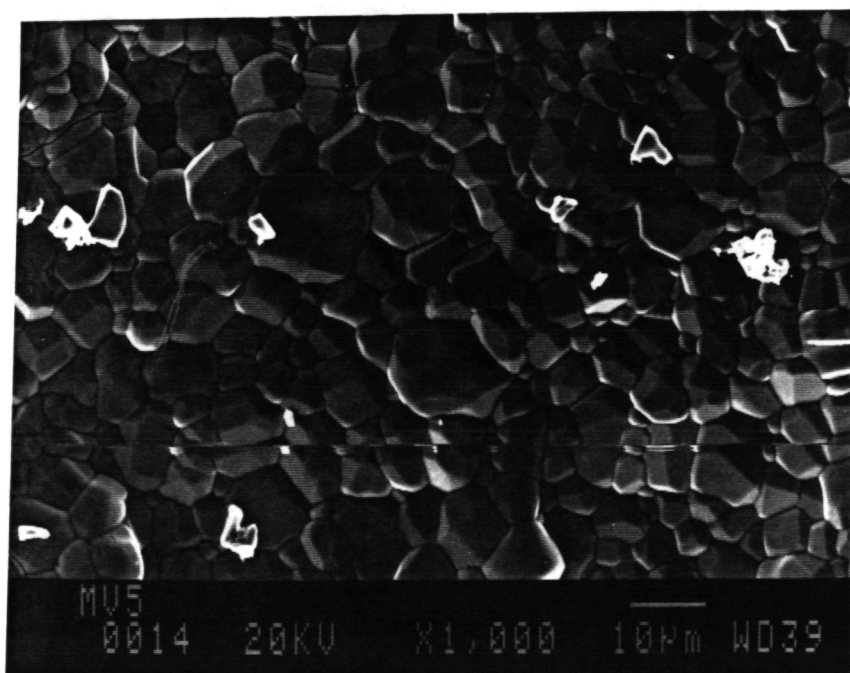
Figure 24. Microstructure of wall at center of Figure 23.

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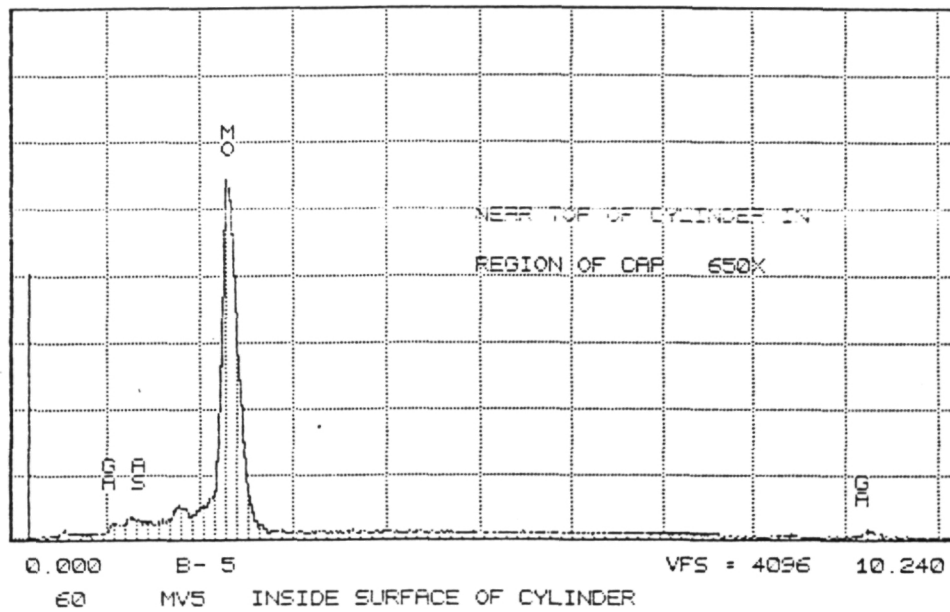
Figure 25. EDX spectrum from wall near top of cylinder in region that was protected by the end plug.
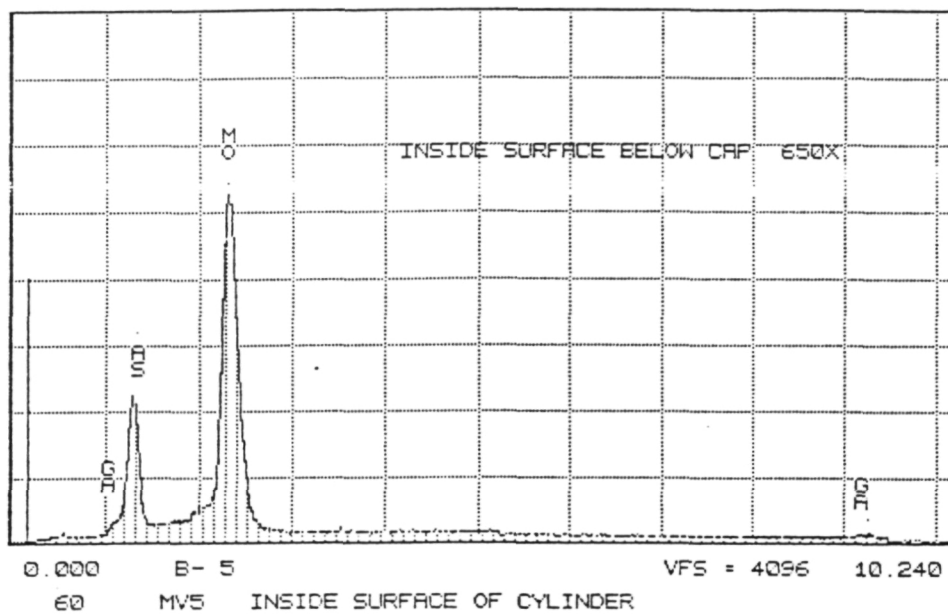
Figure 26. EDX spectrum from wall at region below the cap.
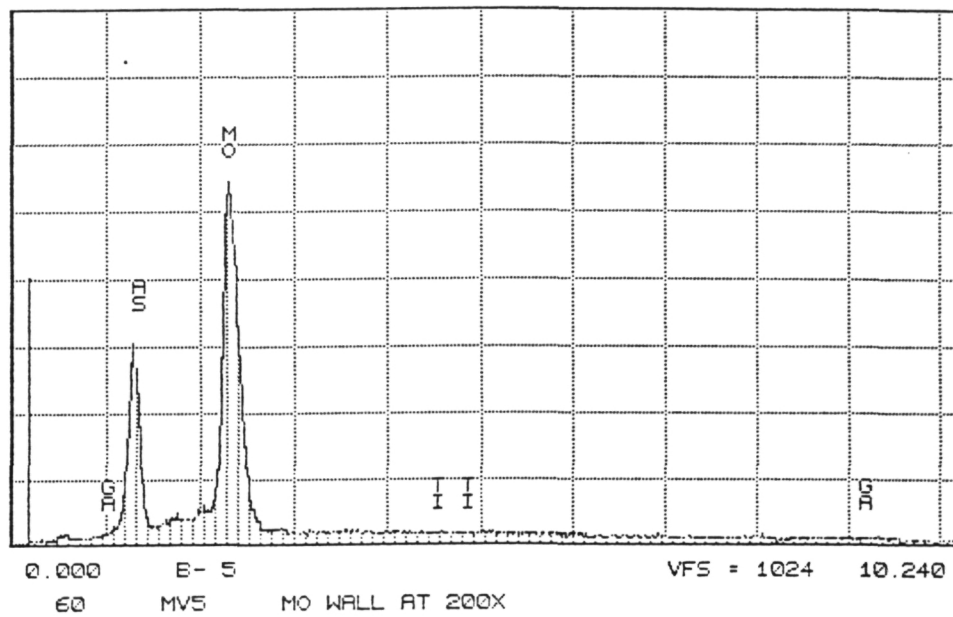
Figure 27.   EDX spectrum from wall in region of Figure 23.

PARTICLE AT JUST BELOW

CENTER OF PHOTO 0013

W   M
     O

W

S U

G
A

T T
I I

W

G   W
A   W

0.000   B- 5   VFS = 1024   10.240

 60   MV5   MO WALL AT 10,000X
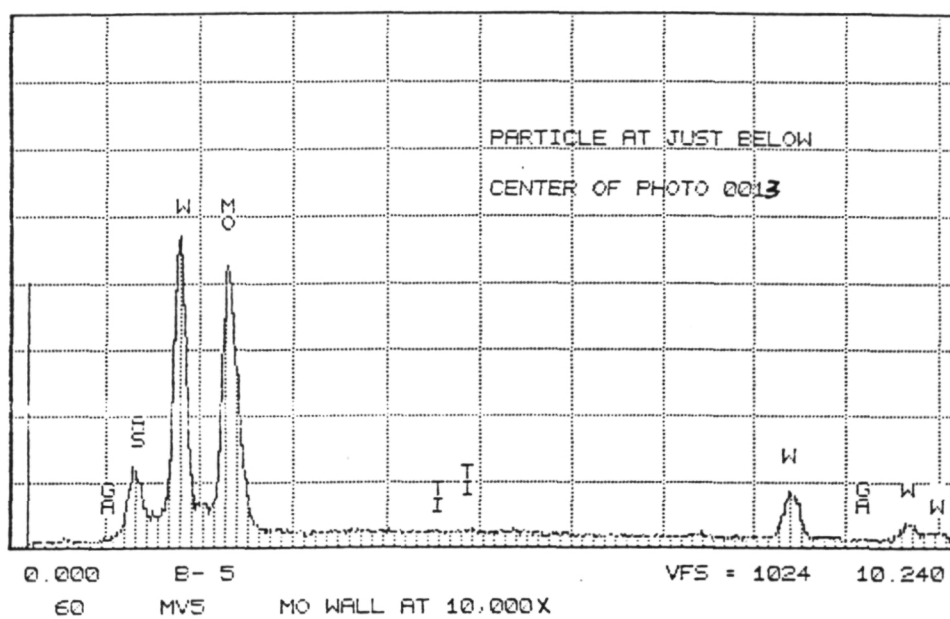
Figure 28.   EDX spectrum from particle found just below center of Figure
23.
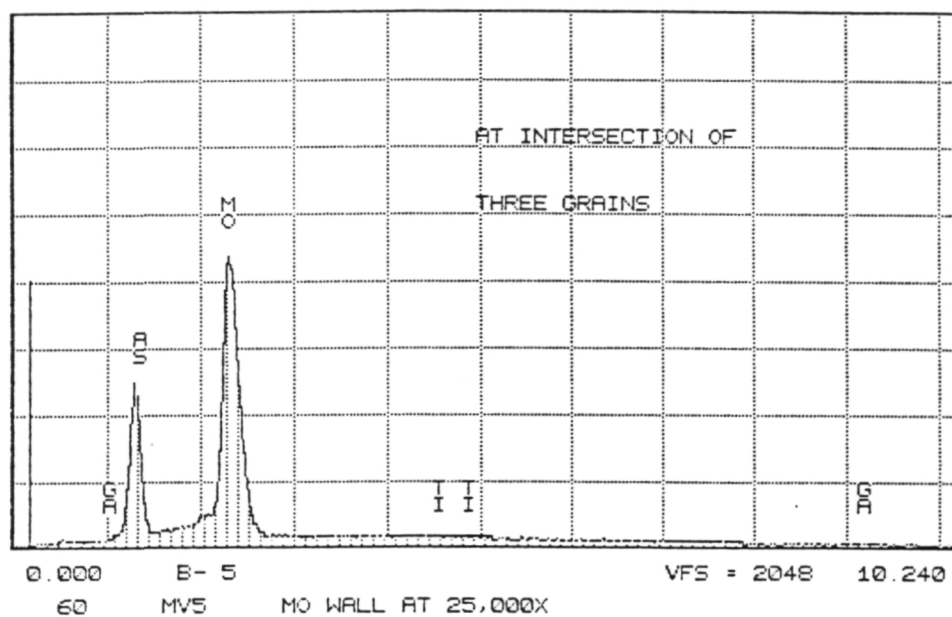
Figure 29. EDX spectrum from the intersection of three grain in wall surface.
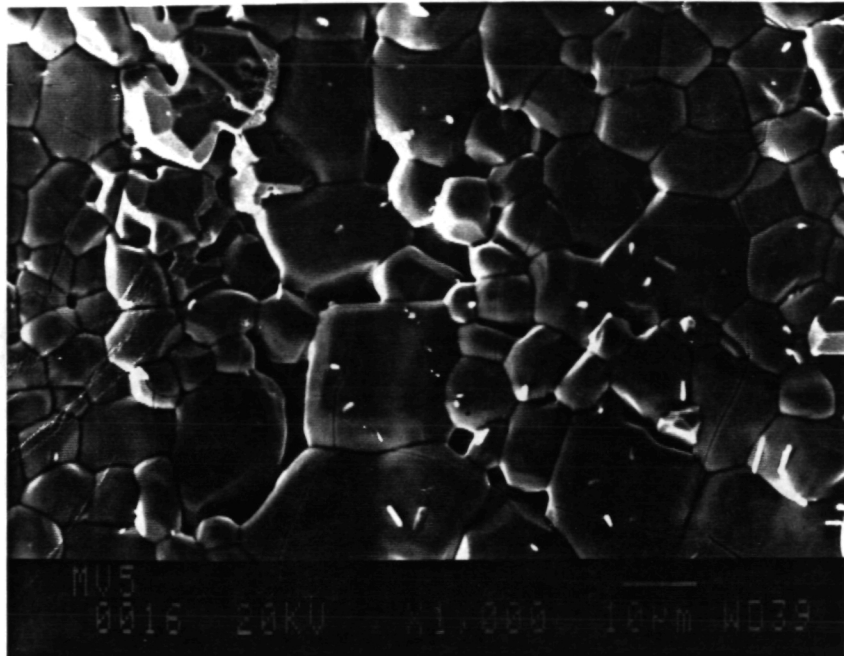
Figure 30.   Microstructure of wall surface at another position than in Figure 24.
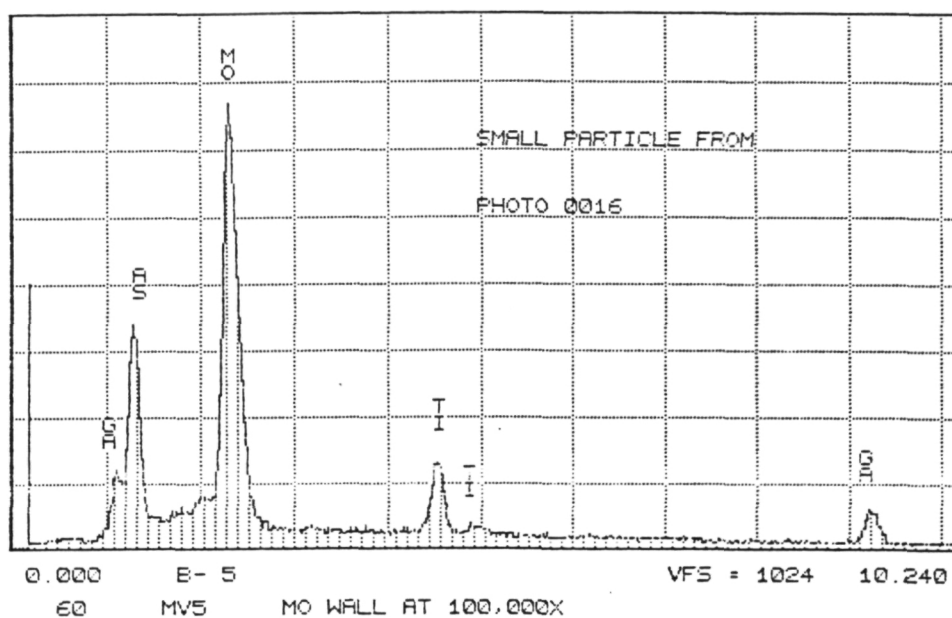
Figure 31. EDX spectrum from small particle found in Figure 30.
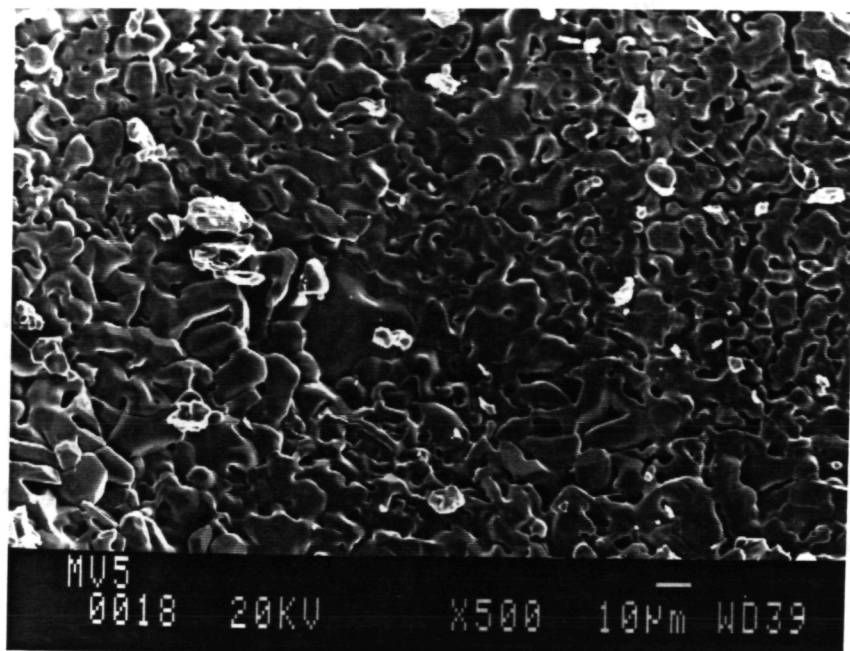
Figure 32.   Structure at the bottom of the reacted cylinder.
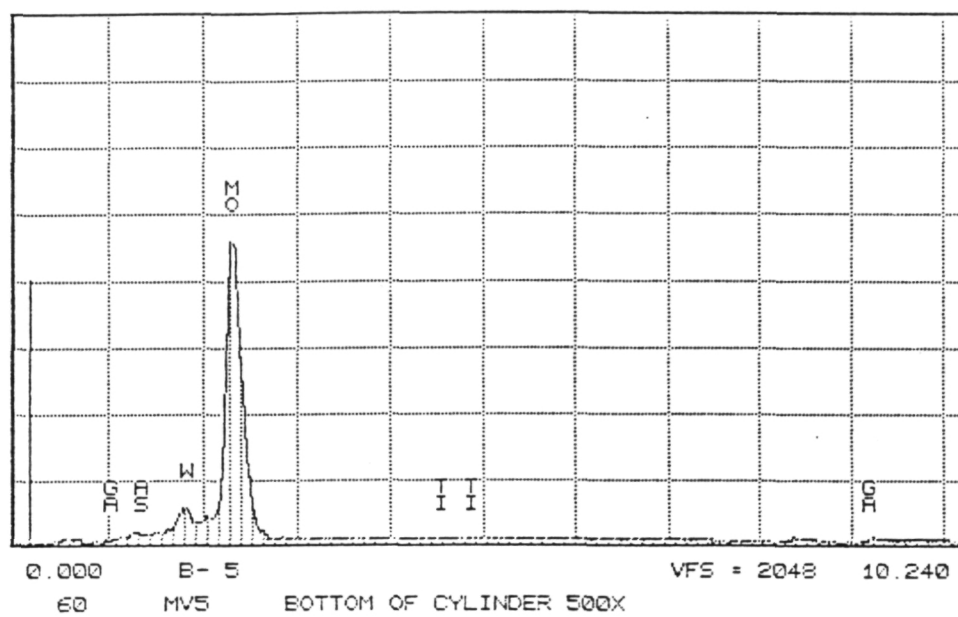
Figure 33. EDX spectrum from bottom of cylinder.
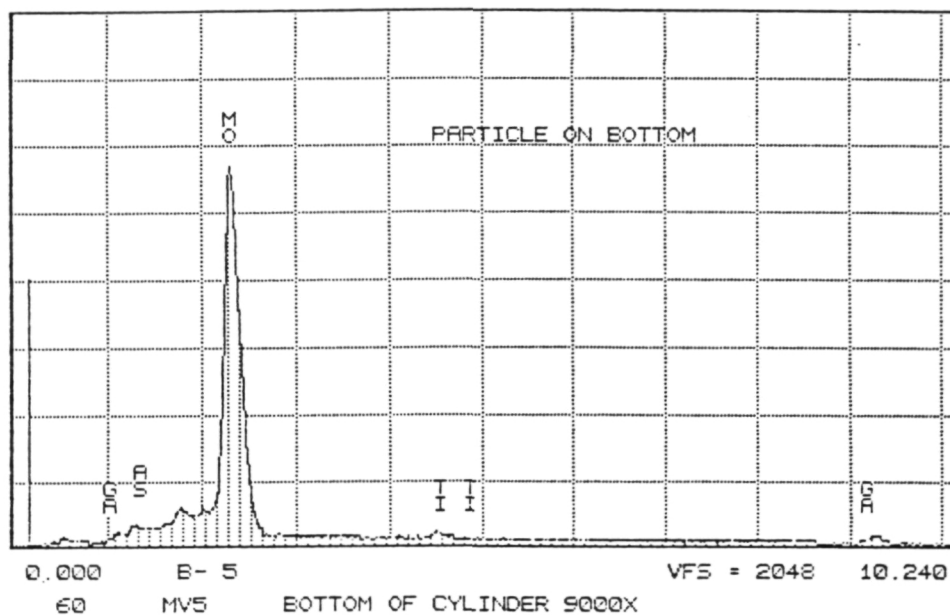
Figure 34. EDX spectrum from particle at bottom of cylinder.
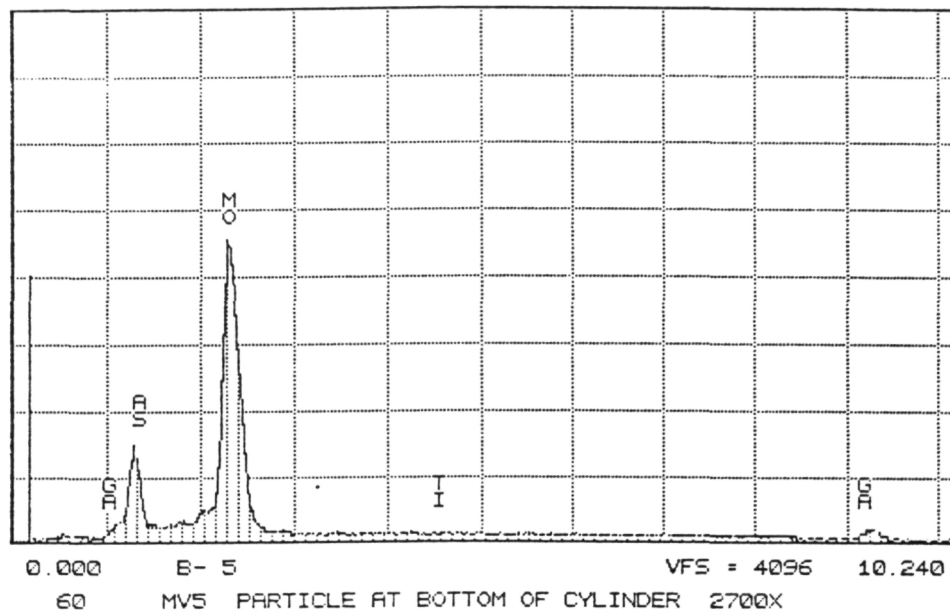
Figure 35. EDX spectrum from particle at bottom of cylinder.
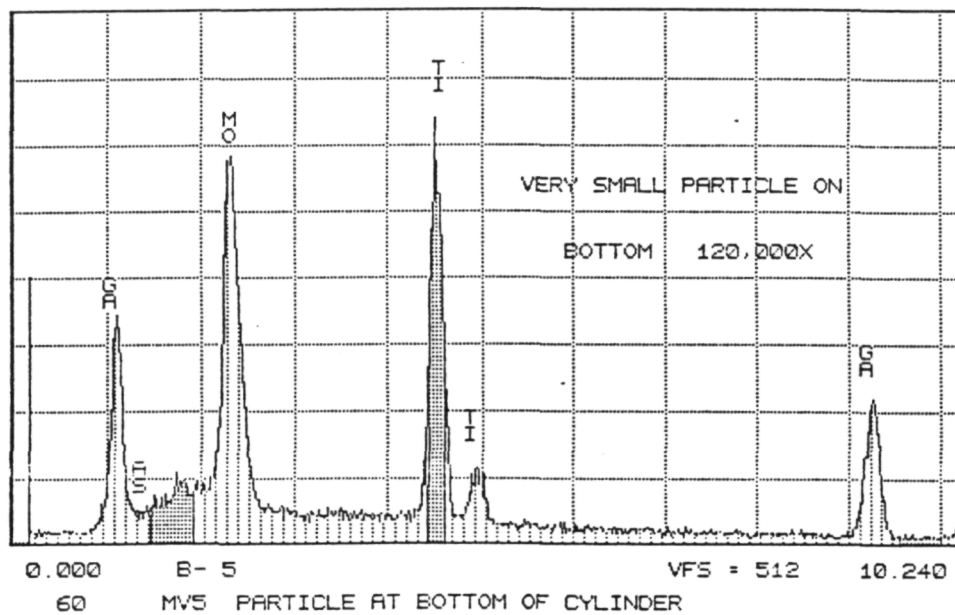
Figure 36. EDX spectrum from particle at bottom of cylinder.
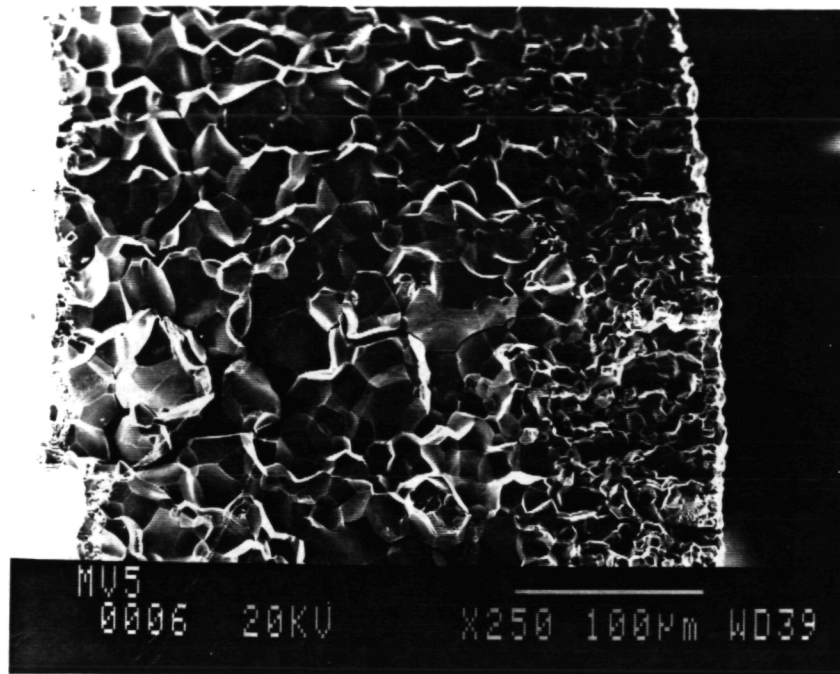
Figure 37. Fracture surface of wall after mechanical breakage. The outside surface is to the right.
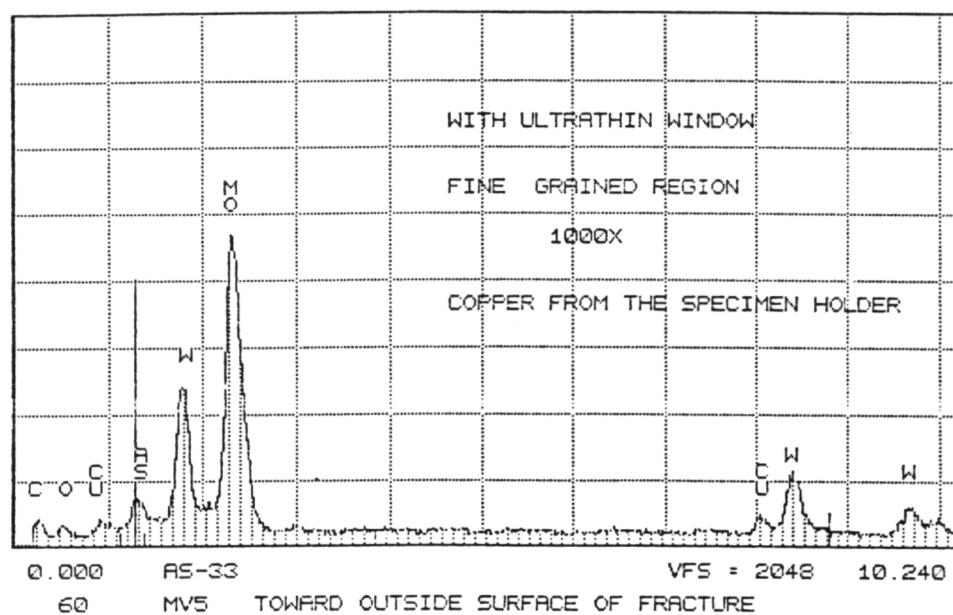
Figure 38. EDX spectrum from region toward outside surface of the fracture shown in Figure 37.
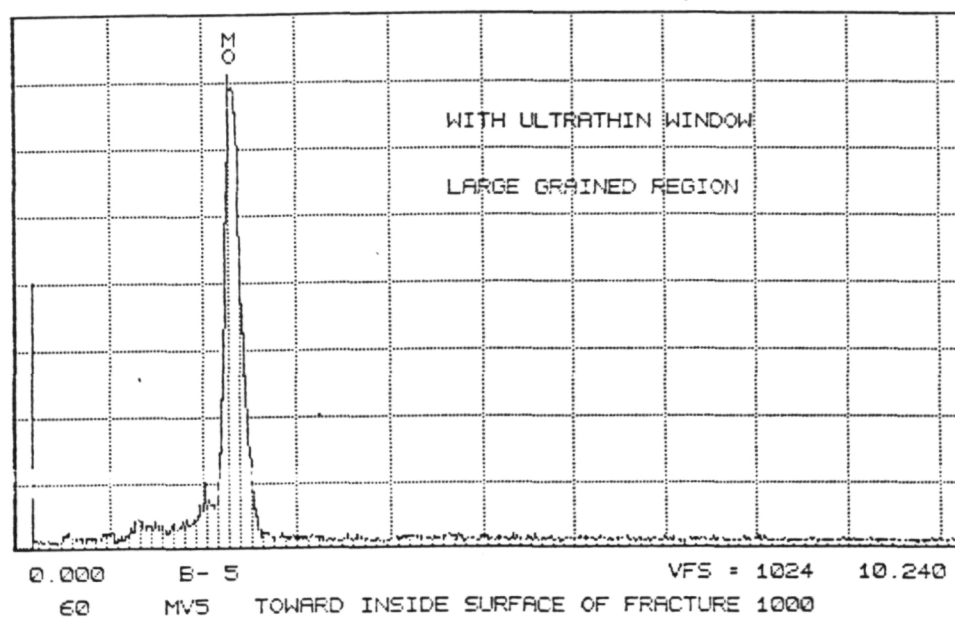
Figure 39. EDX spectrum from central region of the fracture surface shown in Figure 37.
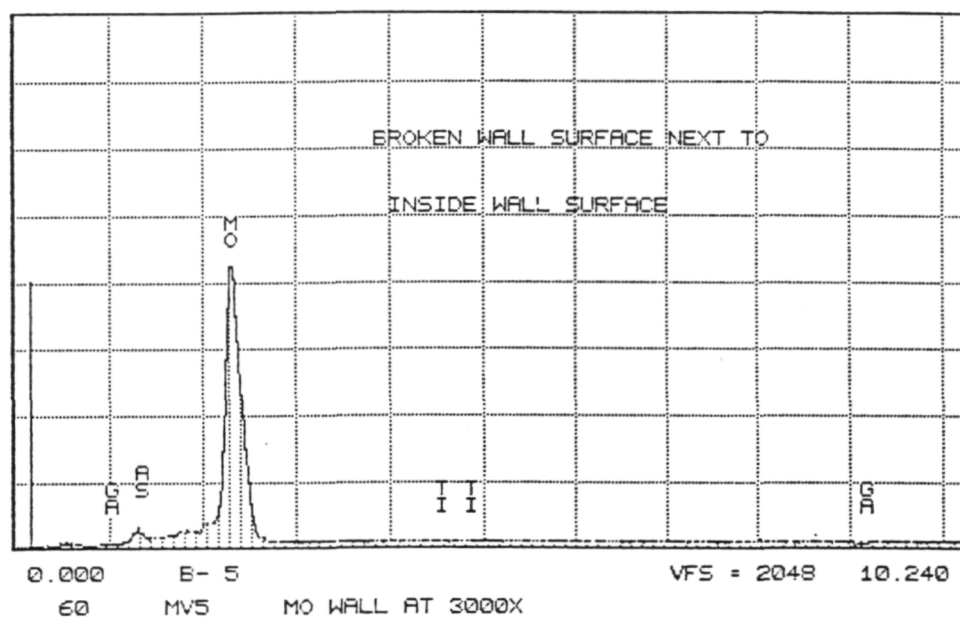
Figure 40. EDX spectrum at region on inside surface of the fracture shown in Figure 37.
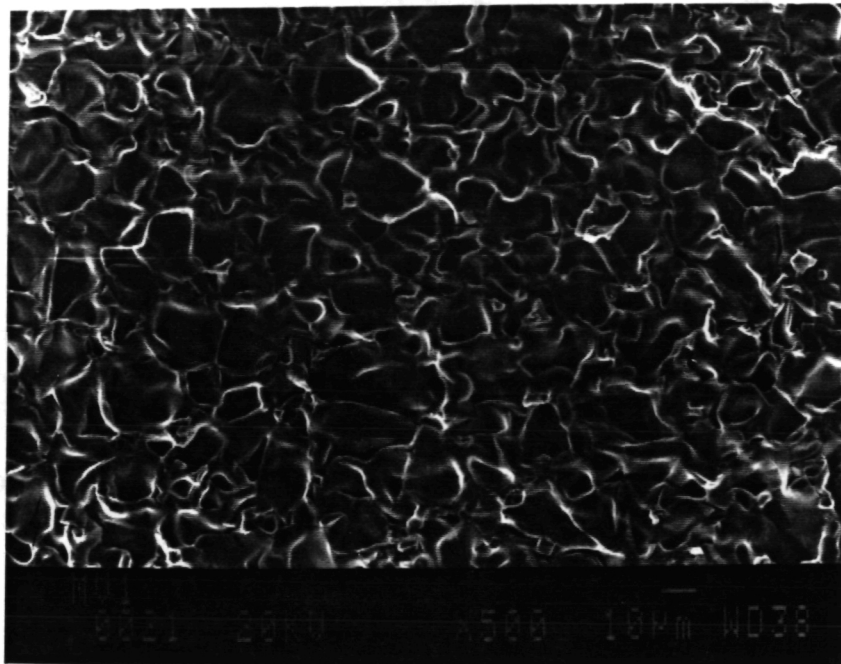
Figure 41.   Structure of TZM treated for 24 hours without GaAs.
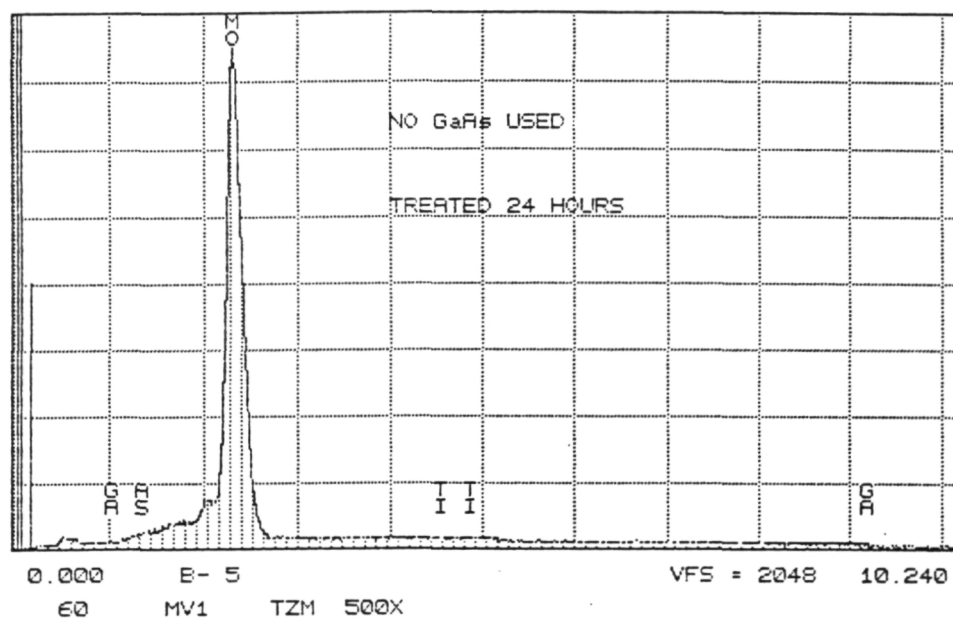
Figure 42.   EDX spectrum from surface of TZM treated 24 hours without GaAs (from Figure 41).
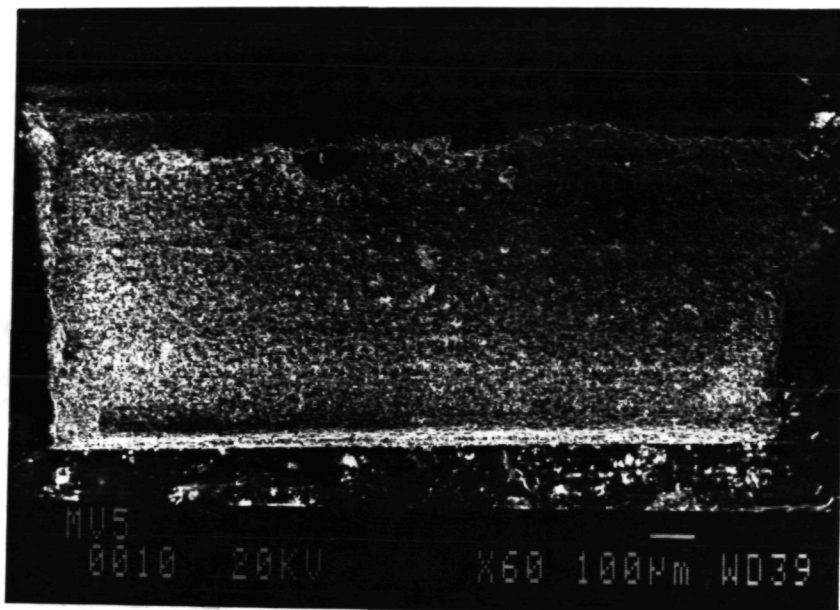
Figure 43. TZM after reaction with GaAs for 24 hours.
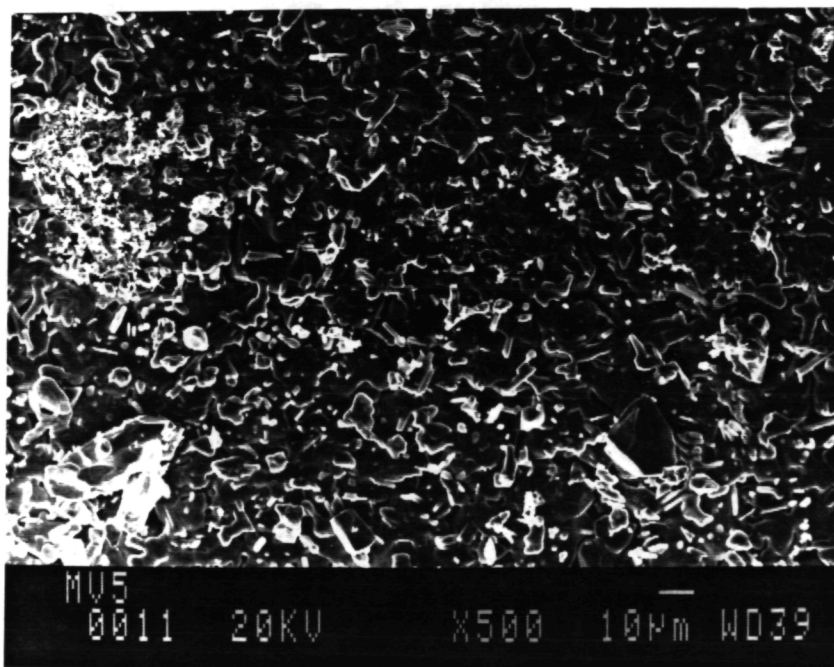
Figure 44. Surface microstructure of TZM shown in Figure 43.
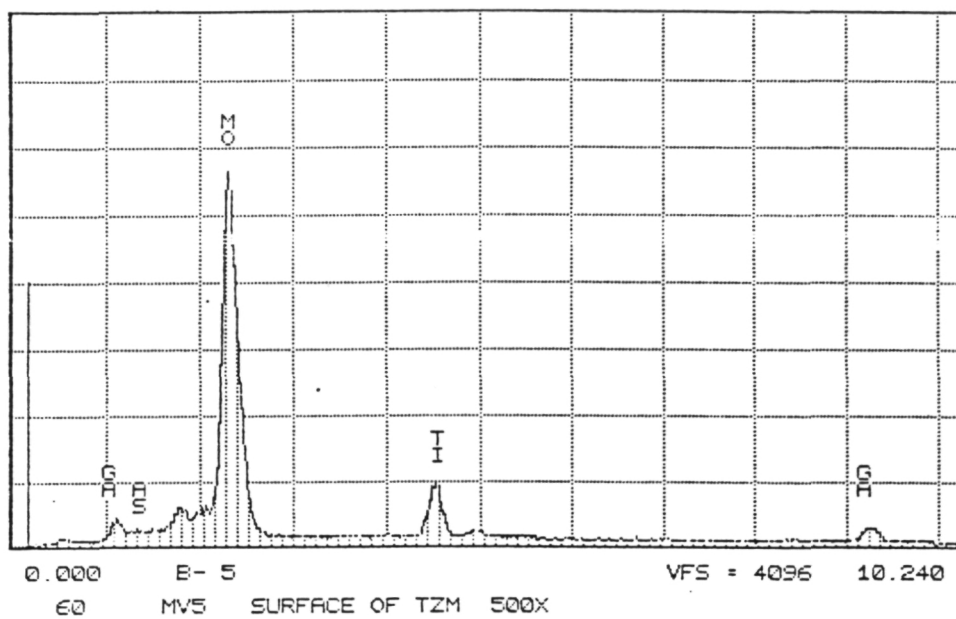
Figure 45. EDX spectrum from TZM surface in Figure 44.

Figure 46.   EDX spectrum from particle at lower right of Figure 44.

TN-5500   THU 18-APR-91   11:12
Cursor: 0.000keV = 0

PARTICLE AT UPPER RIGHT OF

PHOTO 0011

0.000   B- 5   VFS = 512   10.240
  60   MV5   TZM AT 5000X
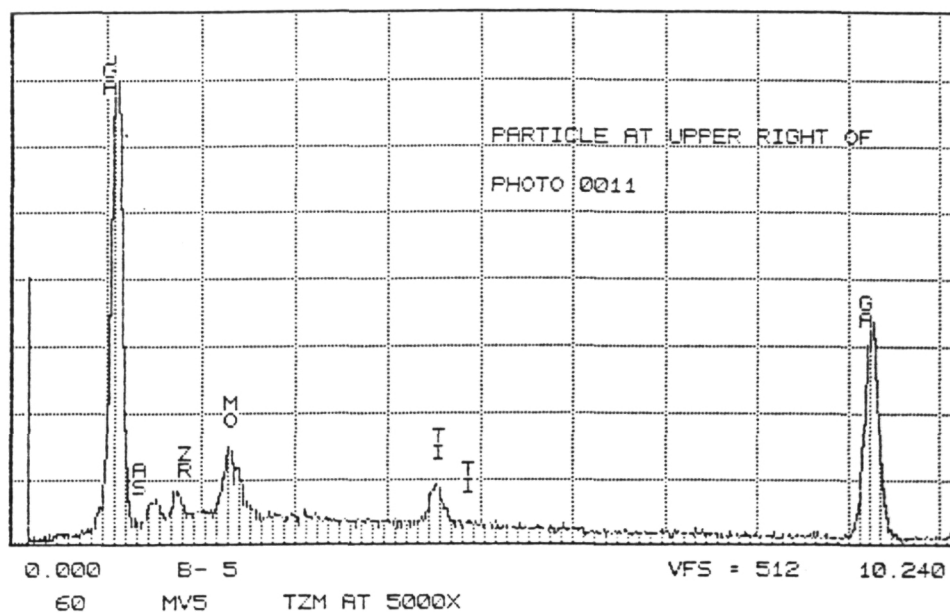
Figure 47.   EDX spectrum from particle at upper right of Figure 44.
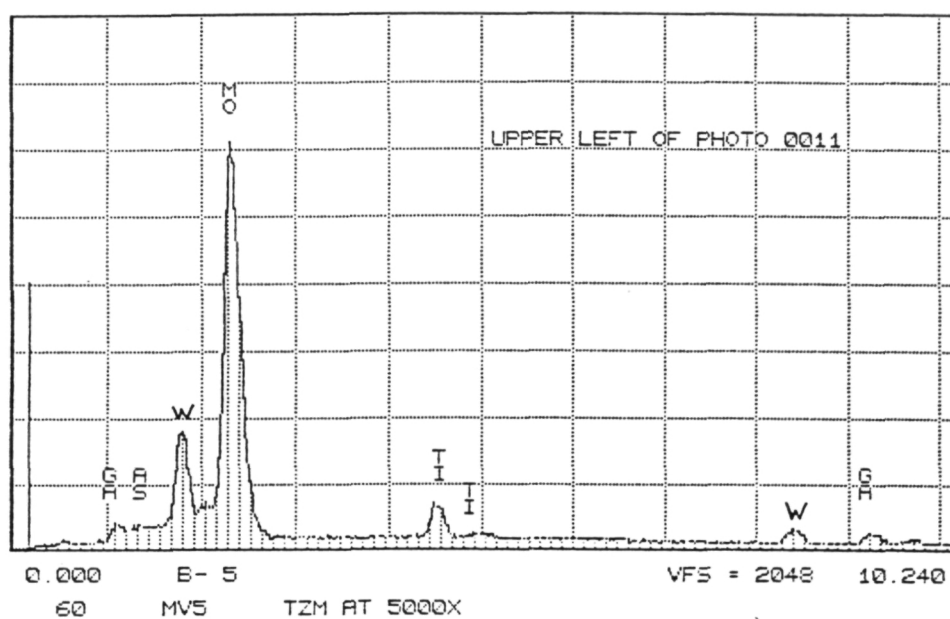
Figure 48. EDX spectrum from particle at lower left of Figure 44.
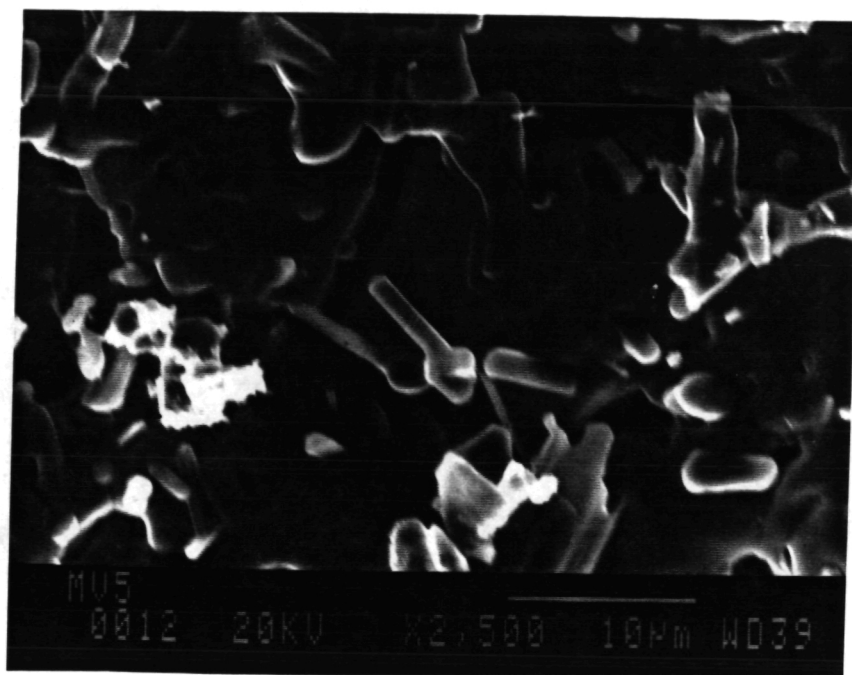
Figure 49. High magnification of center region of Figure 44.
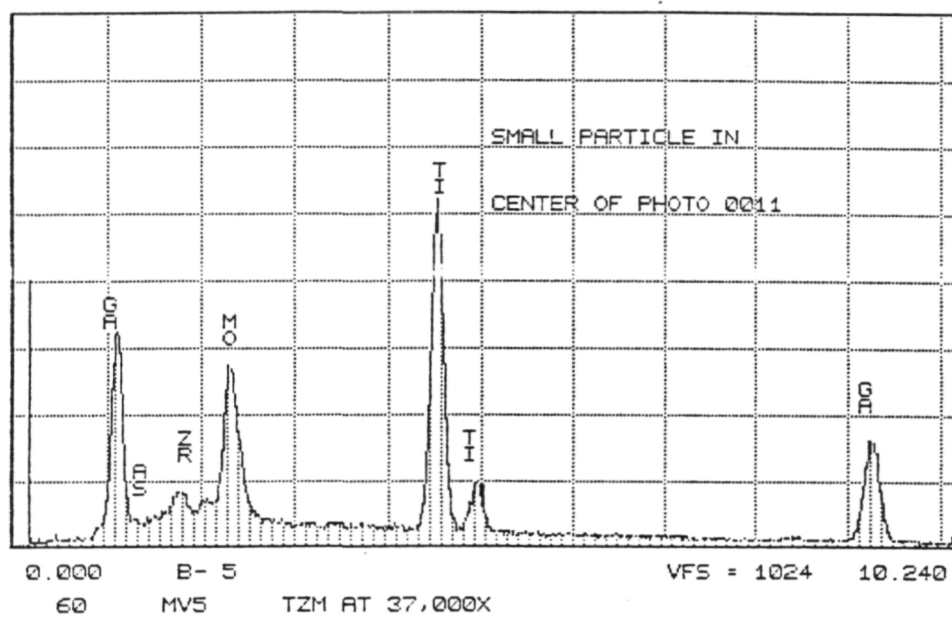
Figure 50. EDX spectrum from small particle in center of Figures 44 and 49.
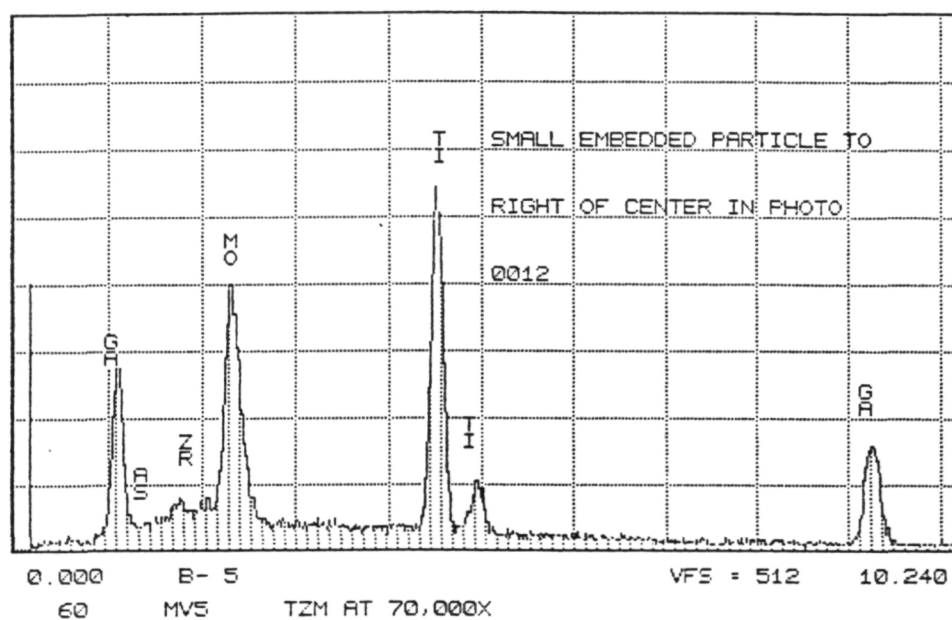
Figure 51. EDX spectrum from small embedded particle to right center in
Figure 49.
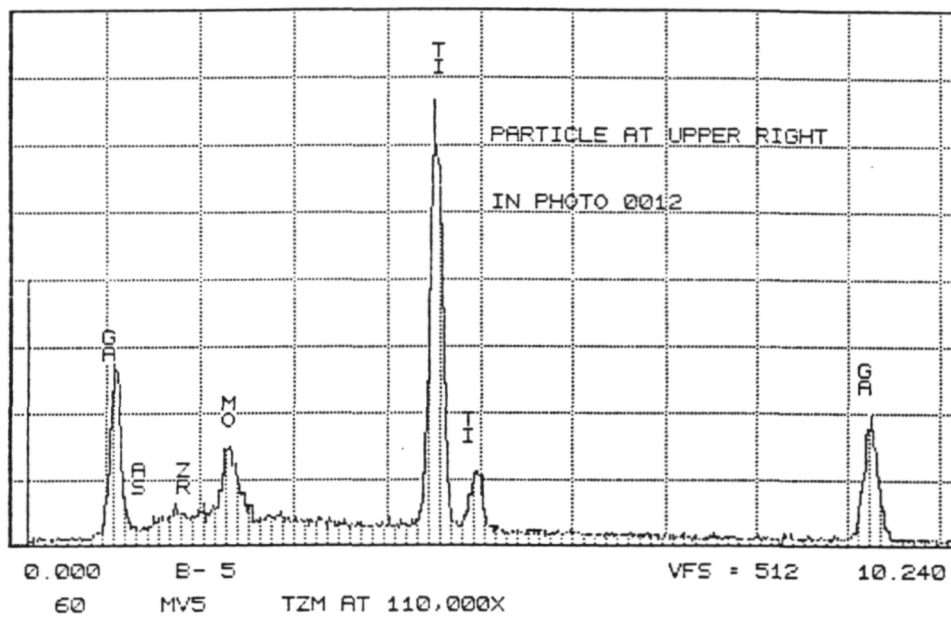
Figure 52. EDX spectrum from particle at upper right in Figure 49.
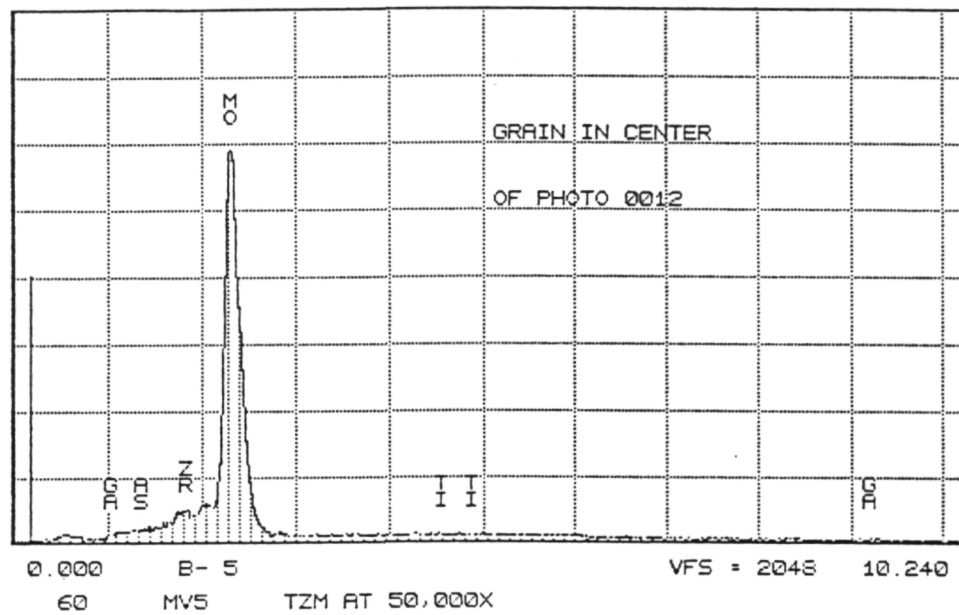
Figure 53. EDX spectrum from grain in center of Figure 49.
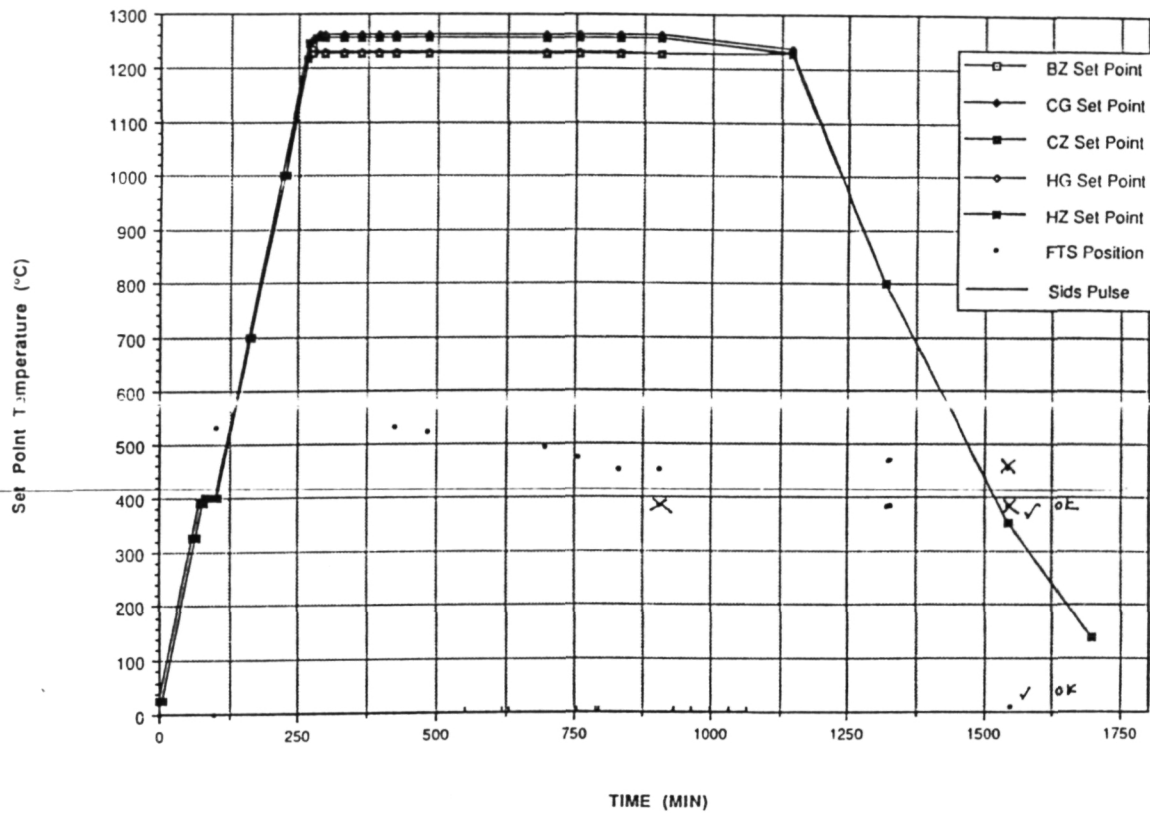
Figure 54. Heat treat cycle for GaAs.
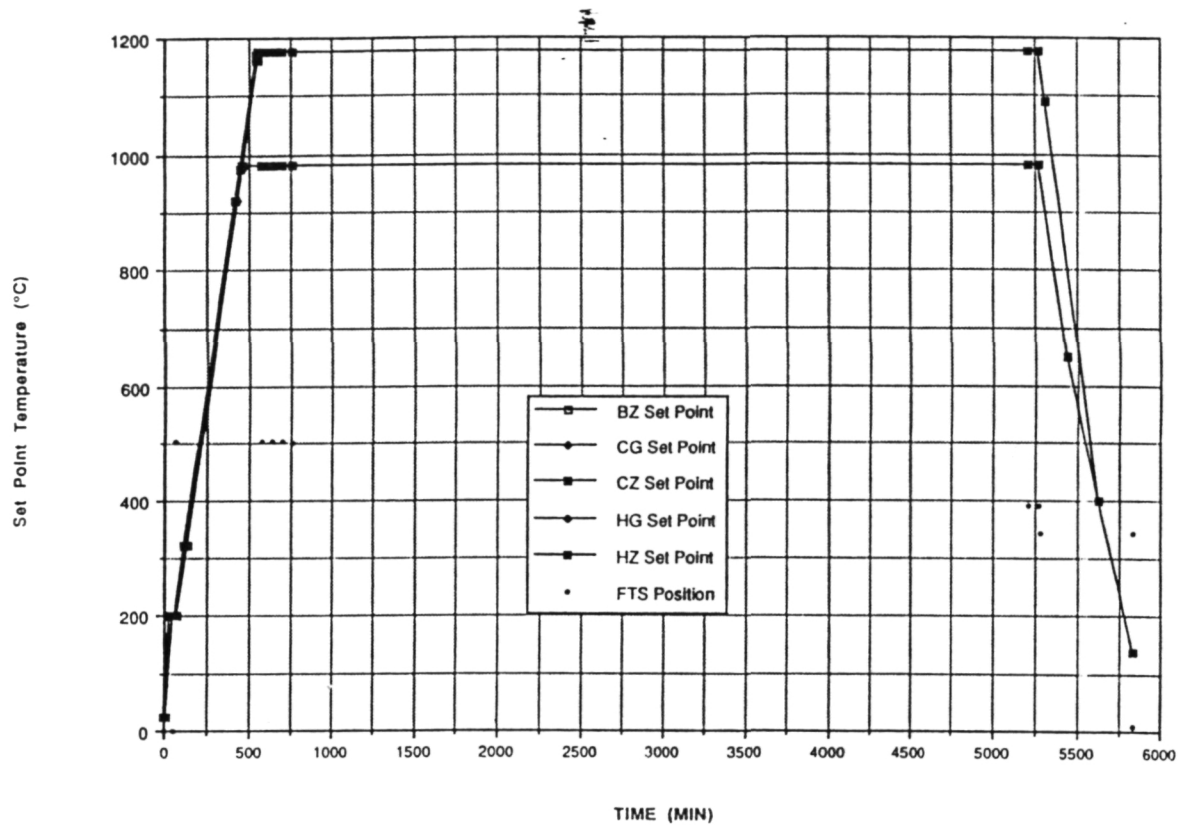
Figure 55. Heat treat cycle for CdZnTe.

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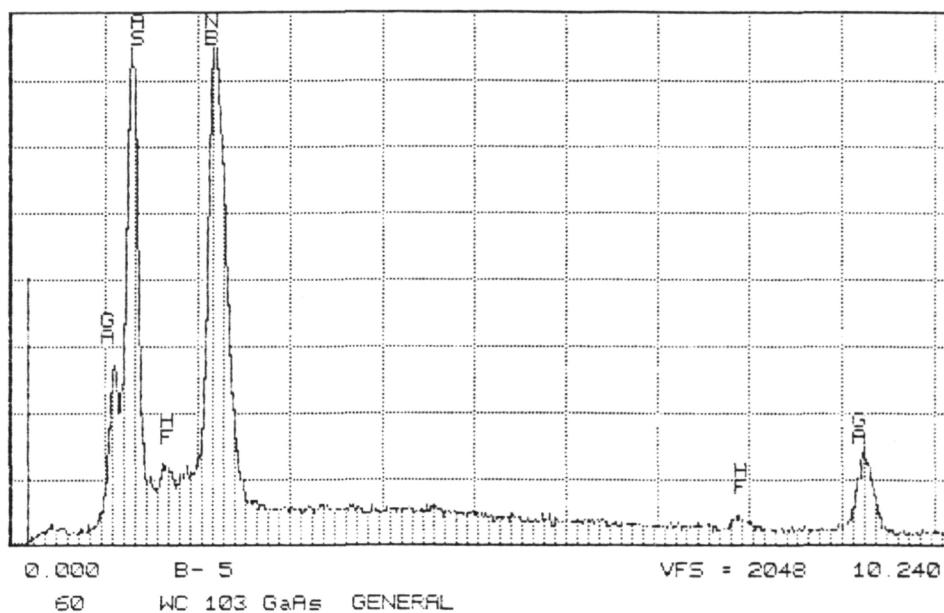
Figure 56. General EDX spectrum from surface of Wc 103 piece with GaAs.

cavity to be filled with melt.

0.219" = 7/32"
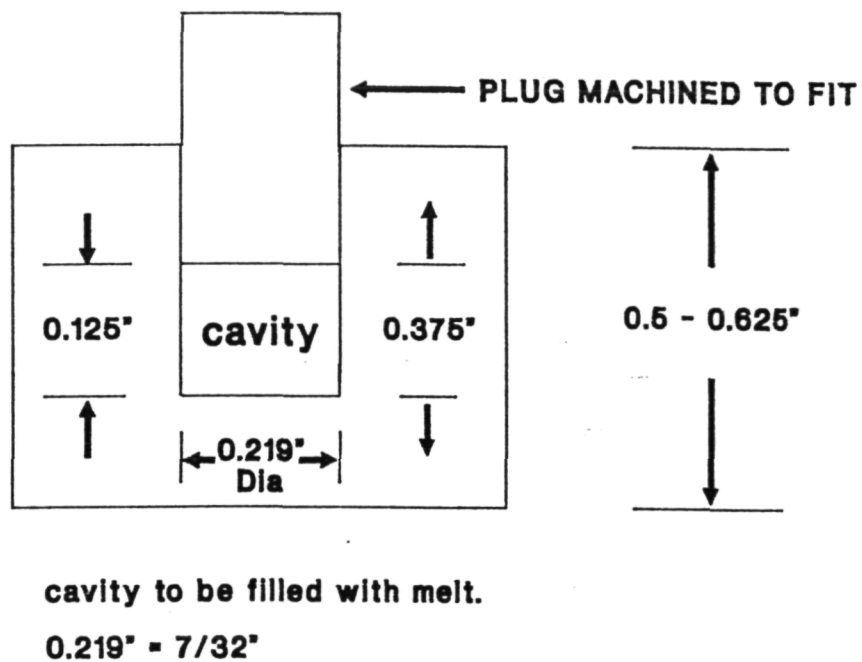
Figure 57. Sample configuration for vertical sectioned samples.
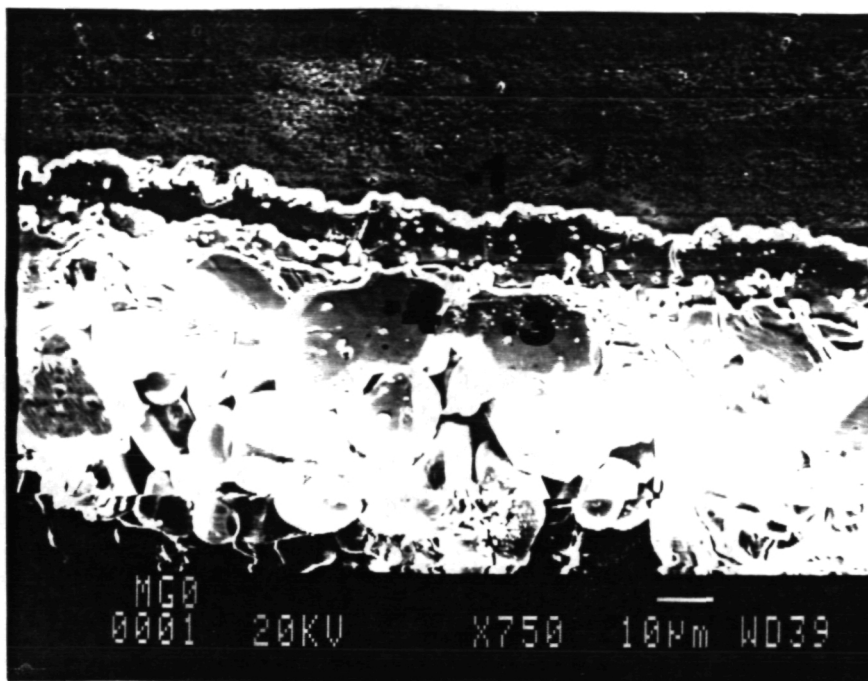
1 - Mo   2 - Mo + little Ga
3 - Mo + As   4 - Mo + As

Figure 58.   Reaction region between TZM and GaAs after 13.37 hr.
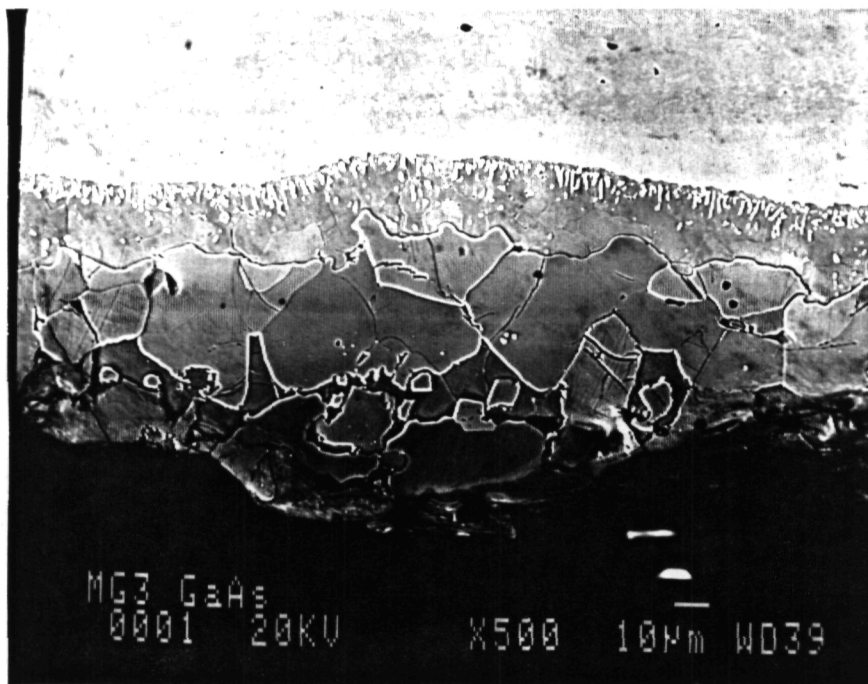
TZM (Mo)

0.022-0.06 mm (0.04 mm ave)
Mo + Ga   White spots (Mo + As)

0.041-0.077 mm (0.057 mm ave)
Mo + As

Cavity

Figure 59.   Reaction region between TZM and GaAs after 28.17 hr.
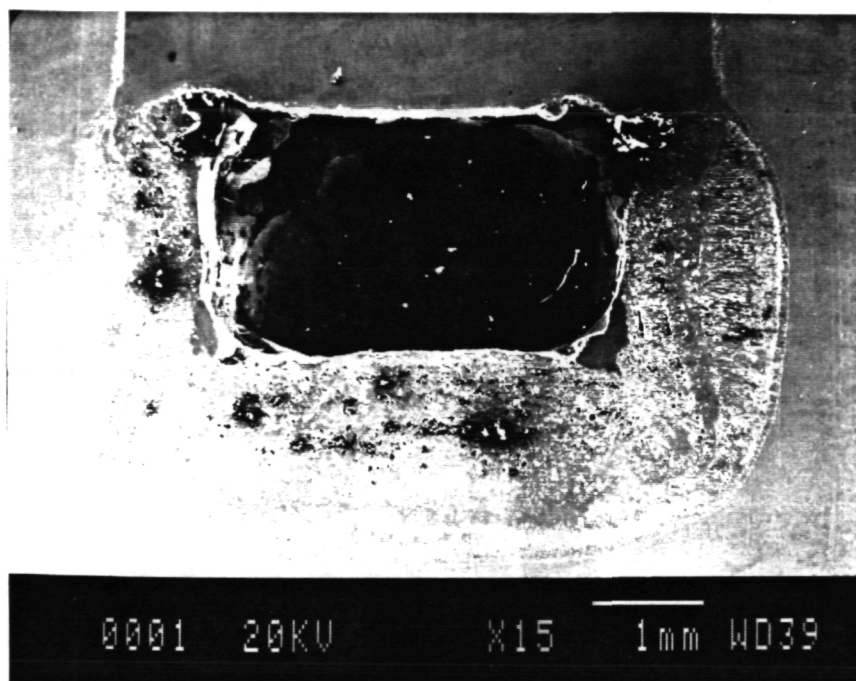
Figure 60. Reaction region between WC 103 and GaAs after 28.17 hr.

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REGIONS
#1 - Cavity in Cylinder
#2 - Unreacted GaAs 0.47-0.67 mm
        0.53 mm ave.

#3 - Reaction Zone 0.27-0.53 mm
        0.36 mm ave (Nb+Hf+As+little Ga)
#4 - Reaction Zone 0.47-0.67 mm
        0.53 mm ave (Nb+Hf+little more Ga
        + much less As)
                #5 - Base metal WC 103
                #6 - Reaction Zone 0.07 mm
                        (Nb+Hf+little Gs + no As)
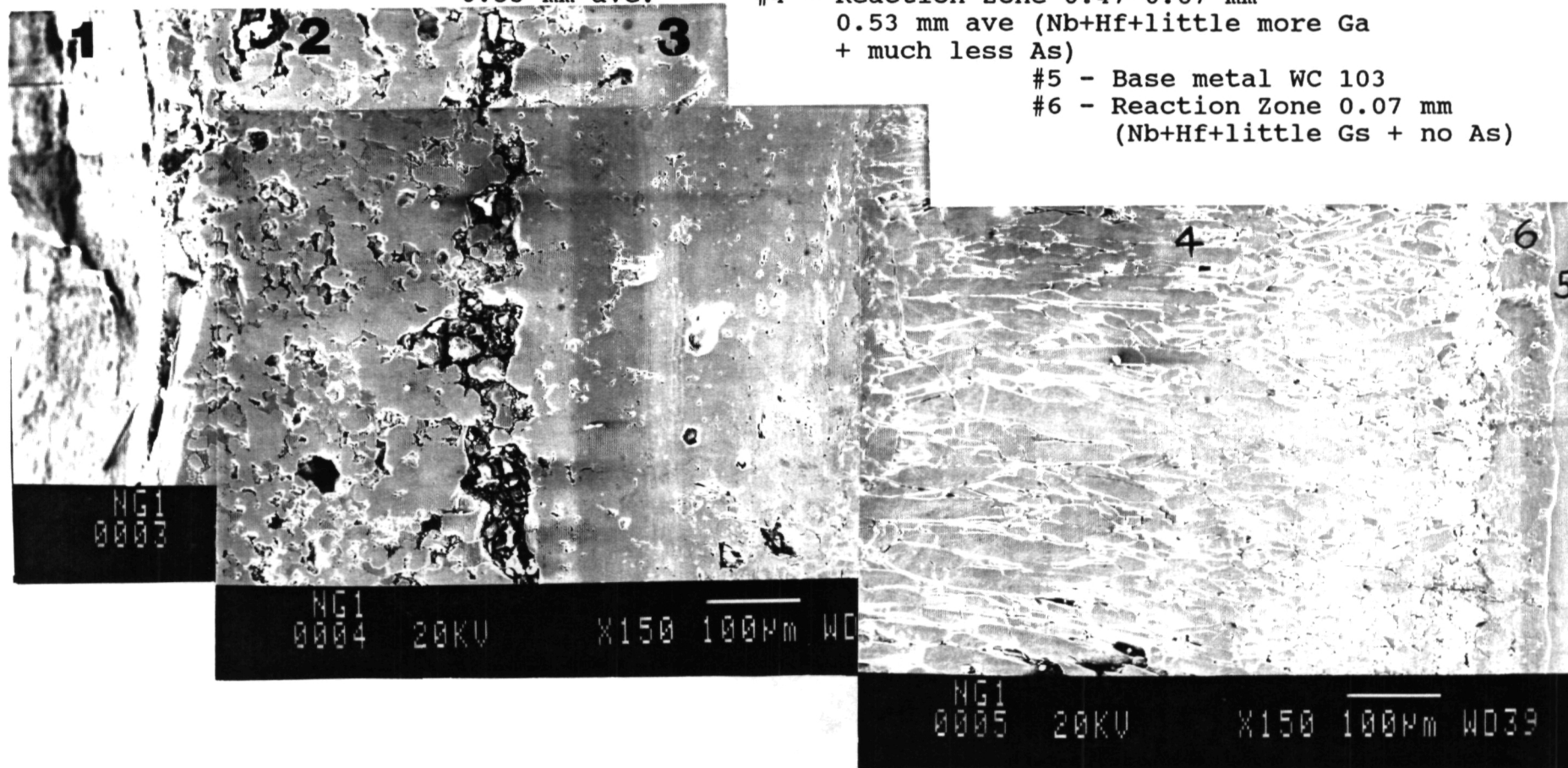
Figure 61. Reaction zone between WC 103 and GaAs after 28.17 hr. (Same region as Figure 60.
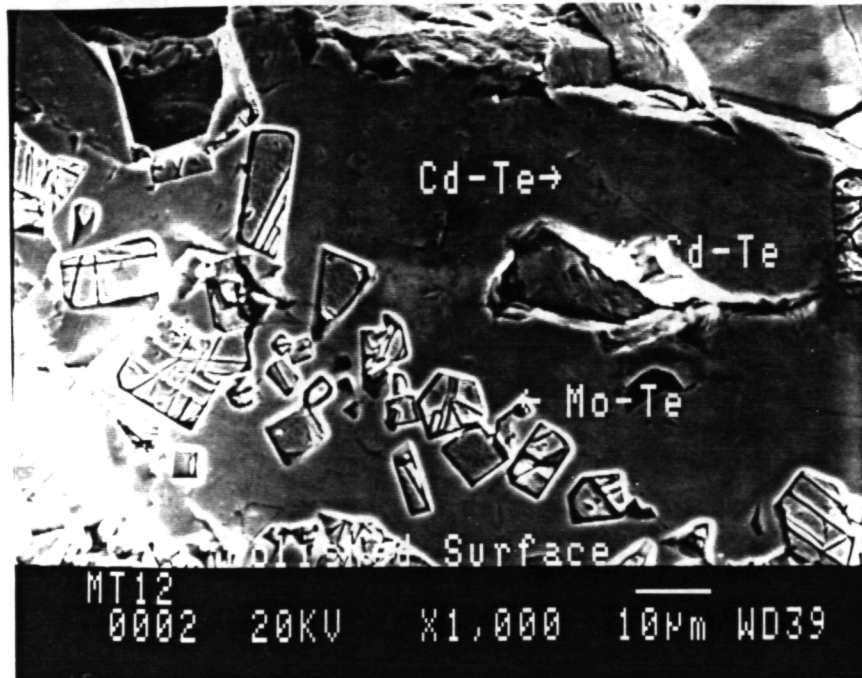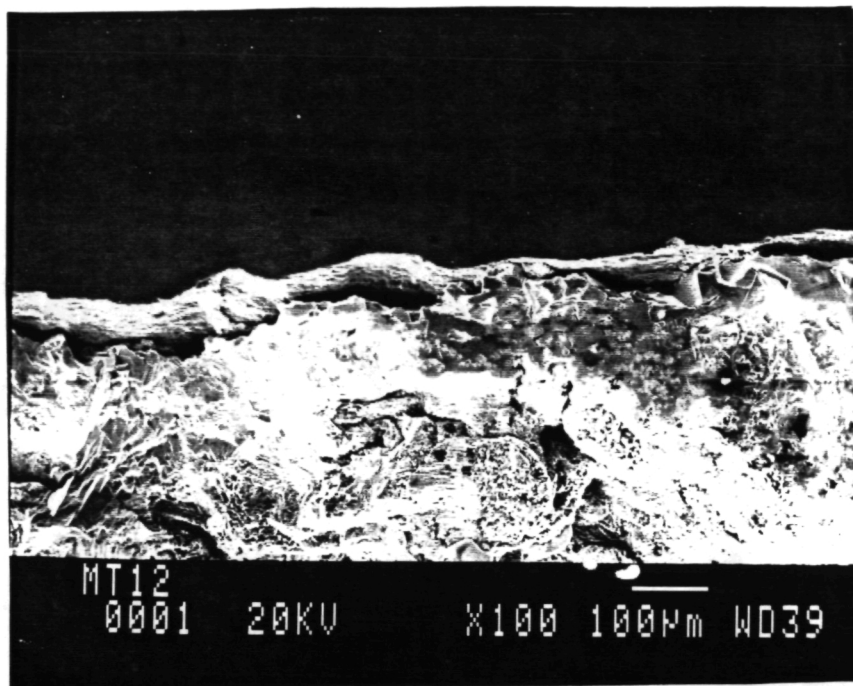
Figure 62. Reaction region between TZM and CDZnTe after 96.67 hr.

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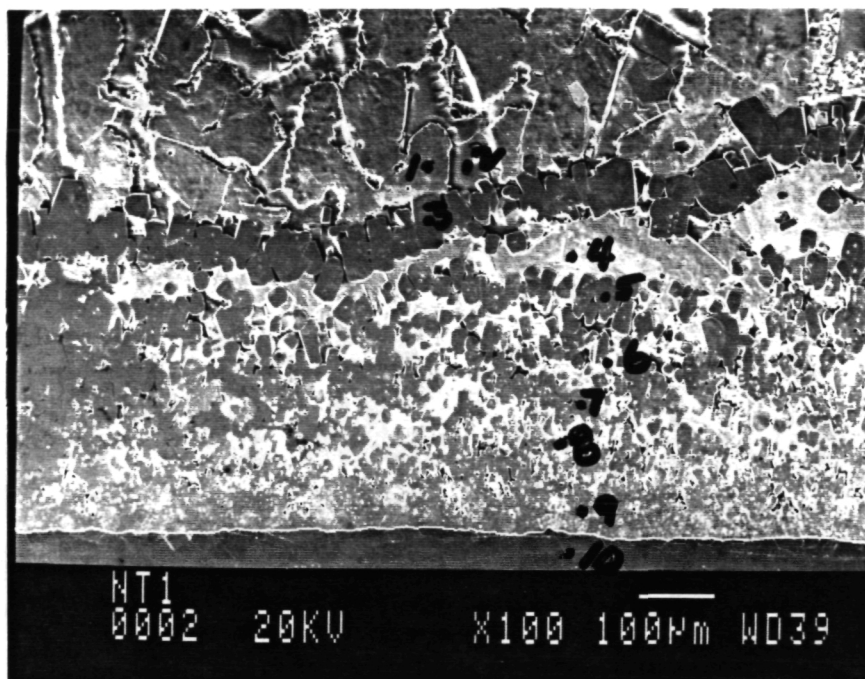
```
1 - Cd + Te                          2 - Cd
3 - Nb + Te + little Hf              4 - Cd + Te
5 - Nb + Te + little Hf              6 - Nb + Cd + Te
7 - Nb + Te + little Hf              8 - Cd + Te + little Nb
9 - Nb + Te + little Hf             10 - Nb + Hf
```

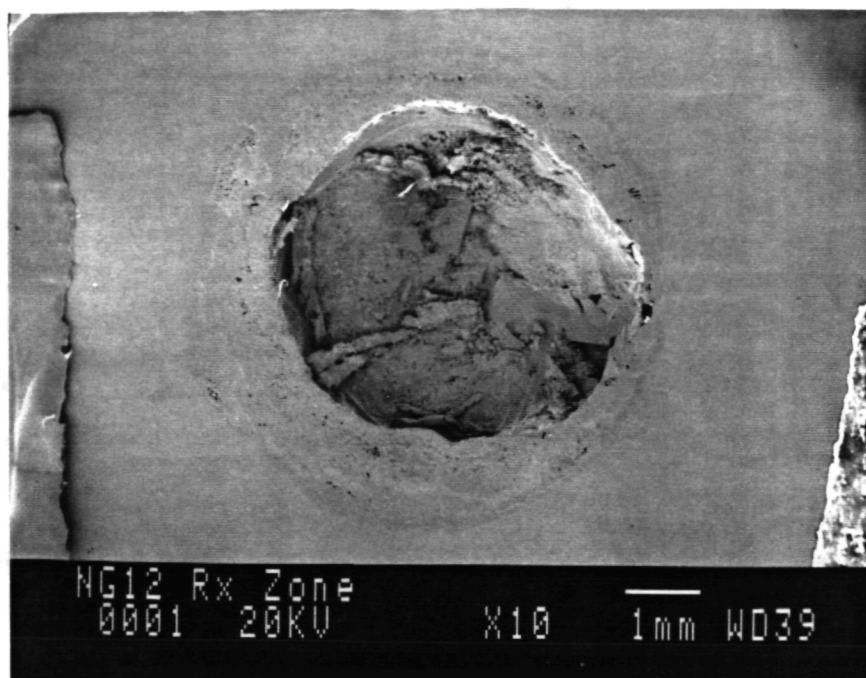Figure 63.   Reaction region between WC 103 and CdZnTe after 96.67 hr.

Figure 64.   Typical appearance of section normal to axis.   Reaction region between Wc 103 and GaAs after 28.17 hr.